

Working Group on the Environmental and Earth Sciences

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1. Introduction and Overview

Synchrotron light sources, primarily in the hard x-ray energy region (4 keV to 30 keV), have had a major impact on research in the environmental, soil, and earth sciences over the past decade and will, in all likelihood, continue to grow in importance in these areas in the foreseeable future. The emergence of the multidisciplinary field now referred to as molecular environmental science (MES) is a direct offshoot of research on environmental-science problems conducted at US. Department of Energy (DOE) synchrotron light sources during the past 5 to 10 years [1]. In the U.S. and Canada, there is an established community of experienced users from MES and the earth sciences that currently numbers about 200. There is also a growing number of new and inexperienced users from a variety of fields who fall under the MES heading. This expanding synchrotron user base in MES and the earth sciences requires (1) x-ray energies ranging from the infrared to the hard x-ray, (2) higher flux and higher brightness beamlines, (3) beamline optics that produce microfocused beams for spectromicroscopy and imaging studies, (4) state-of-the-art x-ray detectors, (5) more beam time on a regular basis, and (6) strong user support at each of the DOE light sources.

MES synchrotron-based research is conducted in both basic and applied contexts. Some of the fundamental research areas that have emerged during the past decade include studies of chemical processes at environmental (mineral-aqueous solution) interfaces, usually involving simplified model systems, using x-ray absorption fine structure (XAFS) spectroscopy and photoemission and studies of the interaction of water and metal-ion adsorbates with mineral surfaces using vacuum-ultraviolet (VUV) L-edge spectroscopy. There have also been some important XAFS studies of reaction kinetics that involve direct monitoring of the transformation of contaminant species as a function of time and system conditions. Over the past five years, MES researchers have also begun to use XAFS and microXAFS spectroscopy and other synchrotron-based methods to study the speciation of contaminants in real environmental samples, which are characterized by compositional heterogeneities on spatial scales ranging from nanometers to centimeters. In addition, there have been XAFS and microXAFS studies of phytoremediation processes in hyperaccumulating plants and soft x-ray spectromicroscopy studies of the reduction of iron and manganese oxides by bacteria, of functional groups on humic and fulvic substances, and of the interaction of heavy metals with microorganisms. These more applied studies, which rely heavily on the results of model-system studies for interpretation, have shown that XAFS and microXAFS spectroscopy can provide quantitative information on the speciation of contaminants ranging from chromium to plutonium in contaminated soils, sediments, mine tailings, tank wastes, plants, and organisms that cannot be obtained directly by other means.

In order for the results of XAFS and microXAFS analysis of complex environmental samples to be of real use to the regulators and engineers responsible for environmental assessment, remediation, and management, it will be essential to conduct large numbers of routine XAFS, microXAFS, and soft x-ray spectromicroscopy measurements on environmental samples in the future. Furthermore, there is also much fundamental MES research to be done using these methods to provide the basis for understanding important environmental processes. Thus, there is a pressing need for a number of synchrotron beamlines that are dedicated to these methods and that are permanently staffed and easily accessible to environmental users. There are a number of hard x-ray (4 keV to 30 keV) XAFS stations, as well as several microXAFS and powder-diffraction stations available to this user base on a peer-reviewed-proposal basis at the Advanced Light Source (ALS), Advanced Photon Source (APS), National Synchrotron Light Source (NSLS), and Stanford Synchrotron Radiation Laboratory (SSRL) (about 5.5 full-time equivalent beam stations in 1998 [2]). Within the next year, there will also be

several new hard x-ray beamlines optimized for XAFS and microXAFS spectroscopy at the APS (GSECARS-CAT, PNC-CAT, BESSRC-CAT) and SSRL (Beamline XI-2), which will increase the total number of full-time equivalent hard x-ray beam stations available to MES researchers to about 8.0 in 1999 [2]. However, there is no soft x-ray/VUV beamline at any of the U.S. synchrotron sources that is optimized for and dedicated to MES-type research. One of the primary objectives of this working group was to assess MES research opportunities in soft x-ray/VUV science and the need for a beamline of this type at the ALS. Given the unique brightness of the ALS in this energy region, the ALS is particularly well suited for soft x-ray/VUV spectromicroscopy applications. Given the importance of this energy region in the environmental and earth sciences areas, there is a clear need for such a facility. One of the major recommendations of this working group is that a spectromicroscopy beamline dedicated to MES should be built at the ALS and operated in the energy range of from about 800 eV to 4,000 eV. Such a beamline would provide unique information on the elements with low atomic numbers (low-Z elements, such as sodium, magnesium, aluminum, silicon, phosphorus, sulfur, and chlorine) that dominate the materials comprising the bulk of the Earth's crust. There is also a very clear need for an MES-dedicated ALS spectromicroscopy beamline that can access the K edges of boron, carbon, nitrogen, oxygen, and fluorine, which are also of great importance in the environmental and biological sciences. This combination of beamlines would provide unparalleled opportunities for cutting-edge soft x-ray/VUV MES research at spatial scales and energy resolutions that cannot be achieved at other U.S. synchrotron-radiation sources.

Although this working group focused primarily on MES applications of the ALS, in large part because of the make-up of the working group, there are many interesting and important applications of synchrotron-radiation methods in the earth sciences, most of which utilize hard x-ray synchrotron beamlines. These include: (1) studies of dissolution and sorption reactions at mineral surfaces, especially in contact or after reaction with aqueous fluids, (2) studies of trace element distributions in earth and planetary materials, (3) *in-situ* determinations of the compositional variations and coordination chemistry of metal ions in hydrothermal solutions and in fluid inclusions in minerals at temperatures and pressures characteristic of the Earth's crust, (4) characterization of amorphous geological materials and their analogs, and (5) studies of mineral phases and phase transitions under conditions of very high pressures and temperatures. Some of the most important advances in these domains have only been possible because of the availability of synchrotron radiation. More details on these topics can be found on pages 62 to 65 of the November 1997 report on DOE synchrotron-radiation sources and science by the Basic Energy Sciences Advisory Committee Panel chaired by Robert J. Birgeneau [3].

Several research areas were chosen for special emphasis by the Working Group on the Environmental and Earth Sciences, and the report is organized around these topics. Although our focus is on the ALS and its unique capabilities for soft x-ray/VUV spectromicroscopy and photoemission studies of environmental materials and processes, many of the topics discussed in the subgroup reports require complementary studies using both hard x-ray synchrotron-radiation methods and non-synchrotron methods. The research areas selected were:

1. Environmental Science Applications of the Advanced Light Source

Participants: Sally Benson (Co-Chair), Sharon Borglin, Steve Colson (Co-Chair), Steve Wasserman

2. Speciation, Spatial Distribution, and Phase Association of Chemical Contaminants

Participants: Paul Bertsch (Co-Chair), Susan Carroll, Harvey Doner, Robert Marianelli, Satish Myneni, Hans Ruppert, Dale Sayers (Co-Chair), Don Sparks, Albert Thompson, Tetsu Tokunaga

3. Chemical Processes at Solid-Aqueous Solution Interfaces

Participants: John Bargar (Co-Chair), Gordon Brown, Scott Chambers, Daniel Grolimund, Tom Kendelewicz, George Redden, Paul Smith, Glenn Waychunas (Co-Chair)

4. Actinide Environmental Chemistry

Participants: Ilham Al Mahamid, David Clark (Co-Chair), Norman Edelstein (Co-Chair), Donald Reed, Roland Schulze, David Shuh, Lynda Soderholm, Jeff Terry

5. Microorganisms, Organic Contaminants, and Plant-Metal Interactions

Participants: Sing-Foong Cheah, George Cody, Roland Hirsch, Chris Jacobsen, Geraldine Lamble, Brian Tonner (Co-Chair), Sam Traina (Co-Chair)

2. Subgroup Reports

2.1 Environmental Science Applications of the Advanced Light Source

(Sally Benson and Steve Colson, Co-Chairs)

2.1.1 Introduction

The ALS has an important role to play in addressing a number of national environmental issues, including environmental remediation, hazardous-waste management, nuclear-waste management, global climate change, agricultural sustainability, trace-element cycling in ecosystems, and environmental risk assessment. These problems present major scientific challenges, in part because natural systems are extremely complex at a range of scales from the atomic to macroscopic and field scales. Moreover, the behavior of these systems is determined by a complex interplay of chemical, physical, and biological processes in spatially heterogeneous environments. Many fundamental questions remain about these systems, and our ability to predict their dynamic behavior has been severely limited in large part by the lack of fundamental understanding at the molecular, microscopic, and mesoscopic scales. Fundamental questions that remain include the composition and speciation of elements in environmental samples, the spatial distribution of reactants, the dominant chemical and biological processes, and how competing processes interact to control reaction dynamics. The ALS can contribute to the knowledge base needed to address a variety of environmental issues by providing insight into the mechanisms of chemical processes at microscopic scales (from grain to colloid size) and molecular scales. Specifically, it can support the following types of investigations:

- Analytical chemistry (e.g., direct speciation of constituents in complex and wet matrices).
- Quantification of spatial distributions in microscopically heterogeneous media.
- Process definition in complex systems (e.g., reactive chemical transport).
- Environmental dynamics (kinetics of reactions in natural systems).

2.1.2 Specific Environmental Problems That Could Benefit from Investigations at the ALS

2.1.2.1 Fate and Transport of Contaminants in the Subsurface Environment

Past practices have resulted in the discharge of chemical and radioactive materials into the environment at many sites, thereby giving rise to extensive contamination of soils and groundwater. The use of conventional technology for remediation of federal and industrial sites is often cost prohibitive, and new technologies are sought to reduce the expense and/or time of remediation or stabilization.

The development of improved technologies for mitigating subsurface contamination requires an understanding of the factors that control how fast the contaminants move (mass transport) and the fate of the contaminants (degradation or reaction). At the macroscopic level, hydrologic processes (e.g., fluid flow through porous media) and geologic processes (e.g., sorption on soil particles) play important roles. At this scale, soil composition and heterogeneity have a profound influence on contaminant fate and transport. At the microscopic level, it is important to know the speciation of contaminants, that is, the chemical form of the contaminant (e.g., the oxidation state of a metal, whether the metal is complexed, or whether a contaminant is adsorbed to a surface), the mechanisms of species transformations (e.g., adsorption/desorption, redox reactions, etc.), and the influence of colloidal particles on transport and transformation. Speciation affects not only the transport properties of a contaminant but its bioavailability as well. Some chemical species of a contaminant, zero-valent selenium for example, are not readily assimilated by an organism and consequently have low bioavailability. This is an important factor in setting standards for “safe” concentration of environmental contaminants. Molecular-level studies can provide fundamental understanding and critical information about microscopic mechanisms and macroscopic processes important to the success of remediation approaches. For example, molecular approaches can provide equilibrium constants, reaction-rate coefficients, and transport coefficients that determine the partitioning of contaminants between different phases, their speciation, and the microscopic rates at which equilibrium is attained.

2.1.2.2 Storage of Nuclear-Waste Materials

Fifty years of production of defense-related nuclear materials have generated large volumes (hundreds of millions of gallons) of complex mixed wastes that contain large amounts of radioactive materials, as well as hazardous chemical wastes. The long-term storage of much of these wastes will require converting them into durable solid forms. Most disposal options for the tank wastes use glass as the final waste form. There are still unanswered questions about the best formulation of the glass to meet disposal requirements. While hard x-rays have provided important information about the speciation of the waste elements, little synchrotron-based work has focused on the glass matrix, which is made up of low-Z elements, including silicon, boron, and oxygen, all of which are readily accessible for study at the ALS under a range of conditions. The high variability of the composition of high-level tank wastes provides a major challenge, since one waste-form formulation may not work for all waste streams, although that is the current baseline assumption. Fundamental understanding of the mechanisms of glass formation and of glass dissolution can provide the basis for design of new glass formulations with desired properties. Molecular-level knowledge of the binding of contaminant species in glass and the polymerization and depolymerization reactions important in glass and melts, as well as in the dissolution mechanism of glasses, can provide insight into the chemistry of these systems that improves our understanding of the microscopic mechanisms responsible for phenomena, such as phase separation, enhanced dissolution with ionic aqueous solutions, etc.

Storage of spent nuclear fuel from civilian nuclear-power plants is also a major challenge facing our nation. Geologic disposal is the preferred option at this time, and investigations are under way to evaluate whether Yucca Mountain, Nevada, is a suitable site for long-term disposal. It is a daunting scientific challenge to predict the behavior of the waste package, the dissolution of the fuel rods, and how radioactive materials will be transported to the accessible environment over a period of 10,000 years. Molecular-level understanding of all the important chemical processes would greatly contribute to our confidence in recommending a site for long-term storage.

2.1.2.3 Sustainable Agriculture

The growing global population creates ever increasing demand for more food. Enhancing the productivity of agricultural lands to meet these needs and mitigating consequent environmental impacts will require better understanding of soil/water/plant systems. Molecular-level investigations can be used to improve our fundamental understanding of nutrient uptake by plants, carbon and nitrogen cycling in soils, formation and stabilization of soil aggregates, environmental behavior of pesticides and herbicides, mobilization of trace pollutants in soil systems, and disposal of agricultural waste water and products. Improved understanding of these processes will lead to more efficient use of our soil and water resources, while at the same time minimizing the environmental impacts of agriculture.

2.1.2.4 Global Climate Change

Understanding the terrestrial and ocean carbon cycles is a critical link in predicting the long-term effects of CO₂ emissions into the atmosphere. Most of the carbon in the terrestrial biosphere currently resides in these two pools. Molecular-level understanding of the biogeochemical processes that contribute to the existence and enhancement of these pools will increase our confidence in climate change predictions, as well as help guide policy makers toward effective strategies for mitigating the effects of CO₂ emissions.

2.1.2.5 Trace-Element Cycling in Ecosystems

Past industrial processes and mining activities have led to surface-water discharges of large quantities of hazardous metallic and organic compounds. Stream flows and rivers have transported these pollutants over large parts of our estuaries, coast lines, and stream beds. While these constituents are usually present at relatively low concentrations, it is recognized that many processes can lead to accumulation of hazardous levels in some ecosystems. Processes such as accumulation in sediments, microalgae, and plant litter provide the opportunity for higher organisms to be exposed to unsafe levels of these pollutants. Bioconcentration and biomagnification of hazardous substances is also possible in the food web, leading to high exposure for aquatic birds and small mammals that feed at the top of the food web. Understanding of the processes that lead to accumulation and the bioavailability of accumulated species is a critical issue that will benefit from molecular-level studies of these processes.

2.1.2.6 Air Quality

Understanding tropospheric chemistry is key to any response to national concerns about the effects of energy production and use on air quality. Among the number of important issues, aerosols and their interaction with other components of the atmosphere, such as particulates and oxidants, remain poorly understood. The development of emissions standards and rational control strategies requires a detailed knowledge of the physical and chemical processes at work in the atmosphere. The Earth's atmosphere is complex, consisting of a multiphase mixture of gases, liquid clouds and precipitation droplets, solid ice crystals, and liquid and solid aerosols. The role of heterogeneous atmospheric processes are even more poorly understood; for example, heterogeneous processes are now known to play an important role in acid-rain formation and Antarctic-ozone depletion, but they are not understood quantitatively, and the role of heterogeneous processes on oxidant and aerosol formation in the troposphere is even less well understood. The lack of a fundamental molecular-level understanding of important atmospheric processes greatly limits our ability to model the impacts of emissions on atmospheric chemistry and air pollution and to design effective control strategies that have minimal impact on human activities.

2.1.2.7 Ecological and Human-Health Risk Assessment

Development of science-based guidelines for human and ecological health requires a comprehensive understanding of the response of living organisms to insults from radioactive and toxic chemicals. There is thus a critical need for fundamental data on health effects, data that will be an integral component of managing cleanup activities. In the past, animal and tissue studies furnished the primary basis for understanding the adverse health effects of toxic materials and for establishing regulatory guidelines. A new generation of risk assessment will require a fundamental understanding at the molecular and cellular levels of crucial cellular mechanisms and processes to provide a more accurate evaluation of risk and the establishment of genuinely protective statutes and standards. This mechanistic extension is required for both accurate extrapolations at high dose levels in animal studies and the low exposure/dose levels needed to set regulatory guidelines for humans. The one important element in this effort is to provide the structural basis at the molecular and cellular level for the mechanisms, including research in cellular processes involved in genomic protection, cellular response to chemical insults, and the mechanistic basis of bioremediation.

2.1.3 Selection of High-Impact Research Topics

One of the key challenges facing the MES community is to identify experiments that are relevant to the complex systems described above and to develop strategies for applying molecular information to solving real environmental problems. One helpful approach is to examine the hierarchy of spatial scales of importance to these problems. Figure 1 below illustrates the spectrum of important spatial scales and how the experimental capabilities of the ALS can be applied to them. Feedback between investigators working at each of the scales can be used to enhance the relevance of molecular-, micro-, and meso-scale experiments. Likewise, results from such directed experiments will be quickly used to guide field-scale approaches for environmental-problem solving. Establishing collaborations with those working more directly on environmental problems is one of the best ways to select research projects with the greatest impacts.

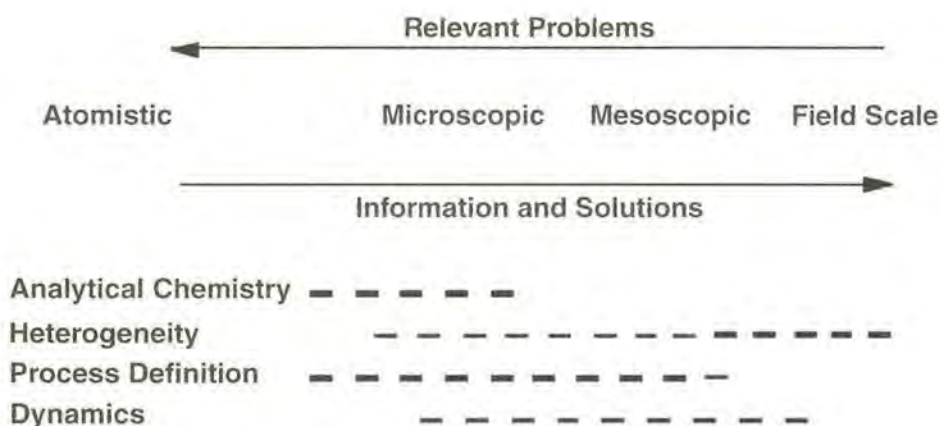


Figure 1. Hierarchy of spatial scales relevant to environmental problem solving.

In selecting high-impact problems, it is important to consider the unique features of the ALS that can contribute to addressing these problems, including the following:

- High flux and brightness in the energy range applicable to the low-Z elements (B, C, N, O, F, Na, Mg, Al, Si, P, S), which include the most abundant elements in earth materials and some of the most important elements in environmental samples.
- Ability to observe natural samples under conditions identical or nearly identical to their original state.
- Ability to examine spatial heterogeneity in natural materials at scales of tens of nanometers to millimeters.
- High spectral resolution for examining the near-edge and extended x-ray absorption fine structure (NEXAFS and EXAFS) spectra of molecules of environmental importance.
- Ability to perform time-resolved spectroscopy on time scales relevant to important environmental processes.
- Ability to perform multiple spectroscopies at different spatial scales and energy ranges on the same sample.

In the last case, soft x-ray/VUV spectromicroscopy and photoemission measurements could be performed at the ALS, and hard x-ray spectroscopy measurements could be performed on the same samples at available hard x-ray beamlines at the ALS or on such beamlines at the APS, NSLS, or SSRL. A standardized sample holder, with easily identifiable fiducial marks, coupled with a standardized sample stage designed to accept the standardized sample holder at MES beamlines at the various light sources would greatly facilitate measurements on the same spot of a sample using different synchrotron-based methods at the four DOE synchrotron light sources. In addition, we foresee a class of user at the ALS who will wish to take advantage not only of soft x-ray microscopes but also of the infrared microscope and the microXAS capability that has recently been demonstrated in the 4-keV to 12-keV energy range.

It is also important to recognize that addressing environmental problems typically requires a multidisciplinary and multifaceted approach to developing solutions and that no single experimental method is likely to provide a unique solution. A variety of complementary analytical methods, including both synchrotron and non-synchrotron techniques, must be used in addressing environmental problems because of their complexity. Hard x-ray synchrotron light sources have proven to be uniquely suited for studying many classes of environmental problems at the molecular level. The challenge presented to this working group is to identify first-order, cutting-edge environmental problems that can be addressed in unique ways using the extremely high brightness soft x-ray/VUV light provide by the ALS.

Important scientific issues will expand across the realms of surface chemistry, analytical chemistry, microbiology, and other disciplines. Even more importantly, there are scientific needs common to all of the focus areas selected by this working group (in Section 1).

Figure 2 illustrates the cross-cutting nature of these focus areas with two of the important environmental problems facing us today. Sections 2.2 through 2.5 provide more information on the opportunities for scientific discovery in each of these cross-cutting scientific topics.

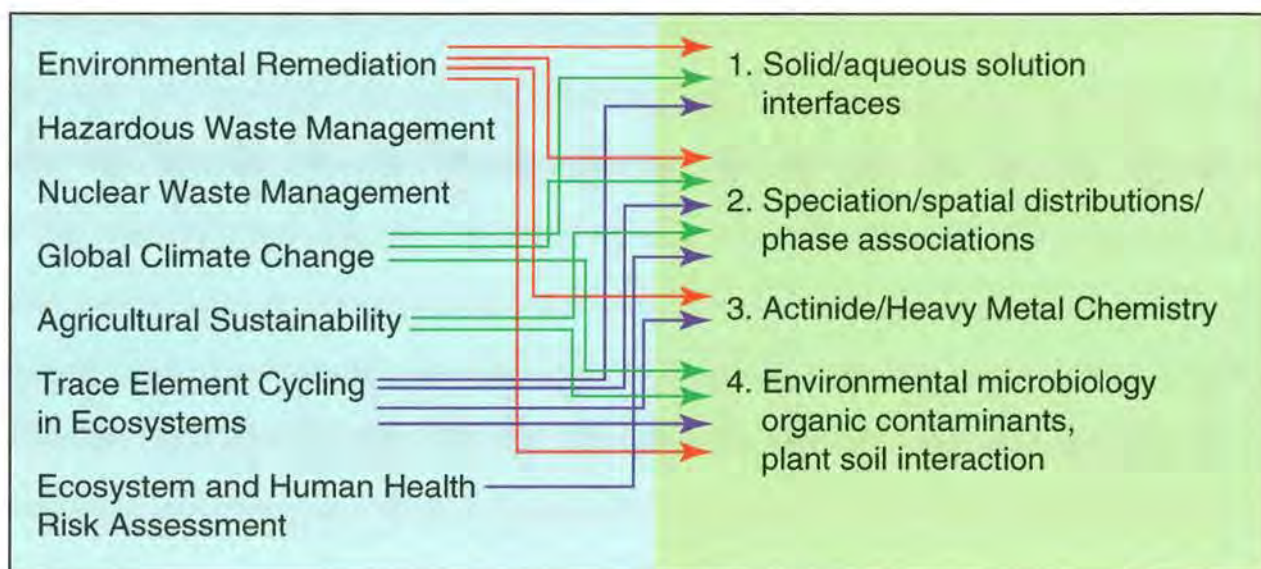


Figure 2. Cross-cutting nature of the scientific areas that form the basis for molecular environmental science.

2.1.4 Meeting the Needs of the Molecular Environmental Science User Community

Making the ALS accessible to the MES user community will require the following:

- High-quality user support.
- High capacity to meet the needs for dealing with the large number of samples commonly used to establish the representativeness of samples/processes and to provide adequate quality assurance.
- A wide range of natural and synthetic model systems representative of natural conditions.
- Rapid data collection and analysis.
- Theoretical support to interpret the spectra.
- Experimental infrastructure to support process-definition and environmental-dynamics experiments (e.g., multi-beamline access, flow-through experimental cells, etc.).

Availability of sufficient beam time is a key question facing the scientific community involved in real-world problem solving. This community must demonstrate that the samples they analyze are representative of the full spectrum of conditions at a field site, which may involve making hundreds to thousands of measurements. Moreover, new analytical tools such as those that could be provided by the ALS are not well known by local, state, and federal regulators. Consequently, they are often not accepted as suitable alternatives to conventional (but more ambiguous) analytical-chemistry techniques. Dealing with this issue will require a multifaceted approach. First, serious consideration should be given to developing dedicated beamlines at several of the DOE-supported synchrotron-radiation sources for high-throughput analysis to meet the needs of this community. Second, scientists who are developing and demonstrating new techniques must first educate the front-line engineers/scientists about the advantages of these techniques and then go with them to the regulators to explain the value in these improved methods. Finally, it must be recognized that we will never meet the needs of the entire environmental-science community for providing these kinds of sophisticated analytical services. Instead, we can work with them to enhance conventional methods of speciating environmental samples, such as sequential chemical-extraction techniques, by validating new techniques.

Another problem in the application of soft x-ray/VUV synchrotron radiation to environmental and geochemical problems is that of the non-expert who requires access to the results of such experiments. This issue relates to attracting new scientists and research problems to the ALS. A two-pronged solution is required. The first is providing easy access to information about a particular experimental station to those who have an interest in performing experiments at the ALS. These additions to the user base will often be seeking to learn whether the ALS can provide new insights into a problem, rather than acquiring immediate results. The infrastructure to support these people must be in place. This includes a designated point of contact for those who are in the exploratory phase of their investigation. The contact should be generally knowledgeable about all of the capabilities of the ALS, and should be able to direct potential "clients" to the appropriate beamline scientist who can provide a definitive answer. At this exploratory phase, a principal investigator working closely with the ALS staff should be able to perform preliminary experiments to demonstrate feasibility of the proposed work. Once the possibility of success has been demonstrated, responsibility for the experiments should shift to the principal investigator. The ALS should be committed, however, to providing adequate user support to ensure that these novice investigators are as successful as possible. It is also essential that the ALS management provide adequate beam time to this growing community of users. The current situation at the ALS results in grossly inadequate beam time allocations to most of the user communities, including the MES/earth-science community.

2.2 Speciation, Spatial Distribution, and Phase Association of Chemical Contaminants

(Paul Bertsch and Dale Sayers, Co-Chairs)

2.2.1 Introduction

It is now widely accepted and well documented with phenomenological observations that chemical speciation controls the mobility of contaminants in the environment, as well as their bioavailability and toxicity. Moreover, it is well established that important environmental interfaces and sorbate/sorbent interactions at these interfaces are among the primary controls on chemical speciation and chemical-species transformations. Over the past decade, there has been an effort to provide fundamental molecular-level information on the mechanisms controlling chemical speciation and chemical-species transformations at mineral surfaces. It has been generally assumed that molecular-scale information on sorbate-sorbent interactions can be used to constrain mechanistic fate and transport models. The utilization of this information to constrain such models at the field and landscape scales has been hampered in many instances by the inappropriate choice of mineral models or by the fact that well-defined monomineralic suspensions often are poor surrogates for natural, multiphase heterogeneous systems, such as soils and wastefoms. On the other hand, molecular-scale investigations of the interaction of chemical pollutants with simplified, well-defined, monomineralic suspensions are essential for unraveling the more complex natural systems, but this approach must be coupled with synchrotron-based studies of the same pollutant species in natural systems. It is only by this approach that information on speciation and chemical-speciation transformations in natural systems can be interpreted.

Over the past few years there has been a steady increase in the number of MES investigations that utilize elemental mapping and spectromicroscopy to interrogate domains within heterogeneous environmental samples via x-ray microprobes and other spectromicroscopic techniques. These studies have indicated that processes occurring at interfaces involving complex mineral assemblages, organic/mineral assemblages, and biological/mineral assemblages, as well as those occurring along pore faces

and fracture linings and in the rhizosphere, control chemical speciation and species transformations over wide ranges of spatial scales. The ability to probe molecular-level environmental processes at grain boundaries, in pores, and along micro- to meso-scale interfaces (e.g., the rhizosphere of plants, which are microbe-rich regions) at environmentally relevant concentrations and the ability to probe the nature of these complex mineral/organic-mineral assemblages are major scientific challenges. X-ray microscopy, micro-x-ray fluorescence, microtomography, and multielement spectromicroscopic techniques are among the most versatile for providing *in-situ* noninvasive elemental-mapping and detailed chemical-speciation information over the large spatial scale required and at environmentally relevant time scales over a wide range of environmental samples (e.g., contaminated soils and sediments, biological samples, wasteforms, etc.). For example, recent applications of synchrotron-based microscale elemental mapping and spectroscopy of zinc, cadmium, and lead in mine tailings from the Tri-State District have provided unique information on the association of these heavy metals with specific types of mineral phases and on the redistribution of zinc and cadmium from primary sulfide phases to secondary hydroxide phases. This type of information is critical for constraining chemical-speciation and contaminant-transport models used to predict the dispersion of heavy-metal contaminants in mine tailings and for realistic environmental risk assessment.

Major scientific issues identified by this subgroup include:

- Molecular-level characterization of important sorbent surfaces in complex multiphase systems, including mineral surfaces and the surfaces of humic and fulvic substances.
- Dynamics of these complex mineral/organic assemblages under varying geochemical conditions.
- Chemical speciation and chemical species transformations of contaminants and other environmentally important elements at environmental interfaces (e.g., mineral grain boundaries, plant root/soil interfaces) and at spatial scales ranging from nanometers to millimeters.

There is a clear need to probe these types of systems with a variety of spectroscopic and diffraction techniques at high spatial resolution (elemental mapping and spectromicroscopy) over a broad energy range (multielement capabilities) at high sensitivity (dilute “wet” systems) and on environmentally relevant time scales (microseconds to hours).

2.2.2 The Potential Role of the ALS in Addressing Problems Involving Contaminants

The ALS offers the environmental and earth-science communities exciting opportunities to begin addressing key scientific questions involving the speciation and transformation of contaminants. One of the greatest challenges in predicting element cycling in natural systems is understanding their chemical speciation and those processes controlling chemical-species transformations. The majority of the Earth's crust is comprised of elements with K edges in the 1-keV to 4-keV range, and the ALS is potentially a world-class facility in this spectral range. Important environmental questions include both natural and anthropogenically accelerated weathering of soil minerals which can be examined by interrogating aluminum and silicon distributions and phase associations in micromorphological features within soil profiles. Other elements of interest to the MES community include boron, carbon, nitrogen, oxygen, fluorine, phosphorus, sulfur, and chlorine. Boron, for example, is a critical nutrient for animals and plants, but it is also a powerful toxicant at elevated concentrations, with a very narrow range between sufficiency and toxicity. In many regions of the world where irrigation is required for the production of food and fiber, boron is the major element limiting sustainable production. Macroscopic sorption experiments have suggested that aluminum- and iron- oxyhydroxide phases in soils are important in retaining boron, as well as in facilitating the nucleation of insoluble

calcium compounds. However, there is no compelling direct evidence to support these phenomenological observations. Elemental mapping at small spatial scales and spectromicroscopy and microdiffraction could be coupled to recent complementary Fourier-transform infrared (FTIR) and pressure-jump measurements to provide the information critical for understanding the behavior of boron over a wide range of geochemical conditions that can be used to develop strategies for reducing or managing hazards related to elevated concentrations. Similar studies with sulfur and phosphorus are required, as are complementary time-resolved x-ray absorption spectroscopy (XAS) sorption experiments on these important oxyanions with soil mineral phases. Other studies examining spatially resolved redox transformations of carbon, nitrogen, phosphorus, and sulfur across redox boundaries could provide insights into important abiotic and biotic processes.

Other important areas of research that can be addressed by the ALS include understanding the distribution and phase associations of elements such as carbon within soil aggregates, as well as the microstructure of the aggregates themselves as probed by x-ray tomography or x-ray microscopy. Humic substances are important yet poorly understood phases in soil that have a major role in controlling the surface chemistry of soil aggregates and the binding of cations. Most of the information on natural organic molecules indicates that they are a complex mixture of organic polymers having a variety of functional groups with a range of protonation constants. Preliminary studies have shown that NEXAFS spectra of the low-Z element (e.g., carbon, nitrogen, etc.) are useful for examining the functional-group chemistry and metal- and contaminant-complexation trends under a variety of solution conditions and on substrate surfaces. Since these organic molecules are ubiquitous in the Earth's near-surface environment where they often coat mineral surfaces, it is essential that we understand the chemistry and macromolecular structures of these compounds. These techniques can also be used to examine the chemical speciation and distributions of organic contaminants in soils.

The coordination chemistry of metal-ligand complexes has been traditionally examined using element-specific XAFS and other conventional laboratory spectroscopic techniques. However, the complexation constants for chemical states of different elements (including contaminants) are still in need of further development. This fundamental information is essential for understanding contaminant and nutrient dispersion patterns in the environment. For instance, the protonation constants of reactions at mineral surfaces, bacteria surfaces, and other biological material-water interfaces are not well understood. In this regard, exploration of low-Z ligands, such as oxygen and nitrogen, using soft x-ray/VUV XAFS methods could provide unique mechanistic information on the factors determining pK_a values and metal-complexation constants. Also this information can complement spectroscopic information obtainable by other methods.

Other critical MES-research areas deal with the distribution and chemical speciation of metal and metalloid contaminants in soils, wasteforms, and biota and those processes leading to chemical-species transformations. Understanding these processes is critical for understanding the fate and transport of contaminants and for designing and evaluating strategies for chemical or biological remediation. Potential areas where the ALS could be used to make unique contributions include spatially resolved L- and M-edge spectroscopy of transition and heavier elements, which would provide detailed information on chemical speciation that would complement elemental-distribution information generated by x-ray fluorescence (XRF) spectroscopy and ongoing studies of K-absorption edge using hard x-ray synchrotron-radiation sources. Preliminary studies have shown that M, N, and (for the heaviest elements) O edges hold great promise in contaminant-speciation studies. These absorption edges can provide complete information on the electronic states of elements that can help in the evaluation of their affinities in complex reactions. Developments in theory should greatly enhance our ability to extract specific information in complex

multiphase systems. Primary examples include studies on oxidation/reduction reactions of selenium and chromium at critical interfaces associated with soil minerals and mineral assemblage. These reactions are important in the immobilization of these potentially toxic elements in soils and sediments, either through natural attenuation processes or as a result of manipulation for deployment of technology for chemical or biological remediation. Simultaneous spectromicroscopy studies of, for example, selenium (L edge), carbon (K edge), nitrogen (K edge), and iron (L edge) within heterogeneous multiphase systems are needed to understand the nature and controls on these oxidation-state transformations in both static and dynamic systems.

2.3 Chemical Processes at Solid-Aqueous Solution Interfaces

(John Bargar and Glenn Waychunas, Co-Chairs)

2.3.1 Introduction

It has long been recognized that adsorption of contaminants onto solid surfaces is a major control on their mobility in surface and ground waters. However, progress in identifying the contaminant-controlling adsorbents has been hampered by the chemical and structural complexity of natural materials and contaminant-adsorbent associations, the dilute concentrations of contaminants in natural environments, and a dearth of techniques capable of probing these systems *in-situ*, *i.e.*, in the presence of water and at ambient pressures and temperatures. Many important natural materials are microcrystalline or amorphous and compositionally variable. Often they occur as coatings on other materials and/or complex multiphase mixtures, with compositional homogeneity on the millimeter down to angstrom scale. To date, *in-situ* synchrotron x-ray fluorescence and spectroscopic measurements in the hard x-ray region have provided a wealth of information regarding the speciation and molecular structures of metal ions adsorbed at solid/aqueous-solution interfaces in model systems. However, x-ray absorption spectroscopy and microspectroscopy investigations on environmentally important elements having K edges in the soft x-ray region (B, C, N, O, Na, Mg, Al, Si, P, S, Cl) have been hampered by the scarcity of intense soft x-ray sources and the practical difficulties of preserving wet samples under high-vacuum conditions. In addition, very few x-ray spectroscopic investigations utilizing natural materials collected from the field have been performed, owing to a general lack of beamlines providing high-intensity focused flux in the soft x-ray region (1 keV to 4 keV). A corollary to this lack of capability is that little is known about some of the components of soils, sediments, or aquifers that are most responsible for the sorption of pollutant and nutrient species. Currently, it is often necessary to assume which matrix components are most reactive when designing model studies of reactive transport in such materials.

With these opportunities and needs in mind, the unique capabilities of the ALS can be appreciated. ALS beamlines provide high flux in the soft x-ray region, the capability to focus x-ray beams to sub-micron spot sizes, and instrumentation to study wet samples in vacuum or low-pressure conditions. For example, with ALS beamlines it should be possible to dynamically follow solid-solute reaction progress involving light elements *in situ* on microscale solid surfaces. We anticipate that this combination of experimental capabilities will drive major breakthroughs in our understanding of chemical speciation and reactions in natural earth materials.

This subgroup identified three overarching challenges in the area of chemical processes at solid/aqueous-solution interfaces that must be addressed in order to model the sources, sinks, and reactive transport of contaminants in the environment and to provide a scientific basis for the design of cost-effective and long-lived solutions to contaminant-remediation and disposal problems.

- What are the environmental solids, including components of multiphase solids, that exert the greatest control over the fate and transport of contaminants in natural waters? For example, what are those solids that have the highest surface areas or highest sorptive capacities for metal ions under common aquifer conditions?
- What are the chemical and physical aspects of the surfaces of these solids that control their interactions with the hydrosphere?
- What are the binding mechanisms and speciation of contaminants, including metal ions, organics, and metal-organic complexes, associated with these solids?

2.3.2 Major Issues Involving Earth Materials and Aqueous-Solid Interfaces

There are three major types of Earth materials with different reactivities that need to be considered and have broad implications for environmental science. Metal (e.g., aluminum, manganese, and iron) oxides and hydroxides, including silicates, are very common as grain-boundary phases and surface coatings on most other mineral grains and have high sorptive capacities for contaminants. Carbonate minerals have very reactive surfaces that can sorb and incorporate toxic contaminants and play a critical role in global carbon cycling. Sulfide materials are electrically conductive and thus can act as electron donors and acceptors in surface redox reactions. They can also be oxidized to release reactive agents, such as sulfuric acid, to groundwater, which often leads to the formation of low-pH groundwater plumes, with subsequent remobilization of sorbed contaminants. Metal oxides, sulfides, and carbonates have varying topological properties, compositional variations, surface defects (e.g., dislocations, stacking faults, growth steps, etc.), and morphologies depending on mode of formation and subsequent alterations. The manner in which these attributes affect reactivity at the mineral/water interface is not well understood, but it is expected to dominate surface reactions. Synchrotron-radiation-based studies alone will not provide the full range of information necessary for complete characterization of these structural, compositional, and morphological features that control chemical reactivity at surfaces, but they will provide essential parts of that information that cannot be obtained using other methods.

It is vitally important to be able to characterize the surface and defect structures in these solid phases in order to (1) understand natural material systems more completely so that heterogeneity and complex structure can be accounted for in geochemical models and (2) develop better model systems incorporating defects and other surface aspects in a controlled manner. This latter consideration is necessary to provide greater control over critical experimental parameters, allow simplification of experimental assumptions, and permit efficient examination of parameter space, which is often necessary for testing hypotheses conclusively. The crucial issues here are identification of the types of defects, their concentration, reactions with water, and reactions with sorbed and other near-surface species. Further, the ability to theoretically model the surfaces and defects is a requirement for interpreting observations and developing a complete picture of the interfacial system.

Several types of surface reactions are important in the control of the fate and transport of toxic contaminants. These include adsorption, surface precipitation, surface-catalyzed redox, and surface-mitigated degradation. Important contaminants include organics, inorganics, and metal-organic ternary complexes, each of which requires specific strategies for detection and characterization. These complexes may be inner or outer sphere, or they may interact with other local species to form precipitates. Effective parameterization of geochemical models is not possible without a knowledge of the reactants, products, and stoichiometries of the reactions involved. Additional reactions include the nucleation and growth of new surface phases or the formation of passivating layers. The formation of passivating layers bears specific attention. Such coatings can restrict further reactions and thus

allow reactive species to be transported far beyond initial sequestration sites. An understanding of surface passivation, and its possible reversal, is needed if accurate models of toxic contaminant transport are to be developed.

Another question closely related to the nature of surface complexation is the nature of the aqueous solution at the mineral/water interface. We do not understand the density, precise composition, or structure of water in the near-interface region. This knowledge is important for accurate models of solvation of species near the interface, the bonding and cohesion of outer- and inner-sphere complexes, and the exchange rates of these species with the aqueous system as a whole.

Finally, much needs to be done to understand reaction rates in decreasing size regimes, including surface transformations, precipitation, and sorption at the nanometer scale, and reactive transport in heterogeneous systems in the grain-size regime (sub-micron to millimeter). Currently, the intermediate or meso-structural regime, comprised of mineral structures, interfacial regions, and co-existing biological entities in the sub-micron to 200-Å range, can only be investigated by transmission electron microscopy (TEM) and other electron-beam, in-vacuum methods that require drying or otherwise altering samples. Analysis of samples on these scales under wet conditions is required to determine chemical gradients, unravel complex heterogeneous mixtures of components, and estimate reaction rates in natural systems.

2.3.3 ALS Applications to Interfaces in Mineral/Aqueous Solutions

2.3.3.1 Characterization of Natural Materials

Most (about 94% by weight) of the surface of the Earth consists of elements whose K absorption edges are in the range from 1 keV to 4 keV. Most of these same species are the major players in natural waters of all types. Hence, investigation of these species in natural materials is fundamental to understanding their chemistry. The ALS bend-magnet source provides high brightness and high flux superior to that at other U.S. synchrotron sources in this energy range at the present time. But more importantly, an ALS undulator source could provide exceptional flux and brightness in this energy range, allowing classes of XAFS experiments not previously possible at these elemental edges. For natural materials, fundamental characterization at the finest possible spatial resolution is needed to understand all of the possible defect and growth structures. This requires both x-ray microscopic imaging and spectromicroscopy capabilities that in-turn require an extremely bright x-ray source. Further, in order to study elements in the range from 1 keV to 4 keV at near-natural compositional ranges, the greatest possible flux is needed. This follows not only from the low abundances of some of the important low-Z elements, but also from the attenuation effects of water and window materials separating specimen and detectors in this x-ray energy regime. An ALS undulator source would be an ideal match for these requirements.

2.3.3.2 Studies of Low-Z Elements

The ALS source provides great advantages for applications involving K edges of the very low-Z elements (boron, carbon, nitrogen, and oxygen). Both ALS bend magnets and larger gap undulator magnets would provide exceptional sources for spectromicroscopy and x-ray microscopy of organic, borate, and nitrate species on mineral surfaces, as well as the interfacial region between mineral grains. Emission spectroscopy can also be employed to aid in identification of particular molecules and characterization of surface geometry, orientation, chemical state, and bonding. These techniques represent tremendous opportunities for the study of biogeochemical processes at mineral interfaces, but they are limited by available technology for beam focusing (zone plates) and detection (scattering effects and very small geometry). Many challenges must be overcome to utilize this opportunity to maximum advantage, including the solution of many daunting experimental problems, the development of improved low-energy high-resolution detec-

tors, the development of new theory to model low-Z x-ray absorption (NEXAFS) and emission spectra, and the simulation of hydrophobic interactions of aqueous solutions and mineral surfaces with accurate electronic-structure theory and molecular-mechanics/dynamics models. This effort will require a broadly multidisciplinary input involving scientists from many institutions.

2.3.3.3 Characterization of Surfaces of Model Earth Materials

Model materials, some prepared with synthetic surface defects, allow a much greater degree of control over experimental parameters than do natural samples; hence models can be used to isolate particular types of interfacial processes. The synchrotron-based techniques currently being used to probe surfaces and interfaces include x-ray standing-wave-induced fluorescence, photoemission spectroscopy, surface and grazing-incidence XAFS, x-ray emission spectroscopy, and photoelectron diffraction. With present U.S. sources, these methods are compromised by low flux and especially by low brightness. However the brightness of ALS bend magnets and particularly of an ALS undulator source would dramatically improve sensitivity throughout this energy range. Even more significantly, methods such as photoelectron diffraction, high-resolution photoemission, photoemission microscopy, and x-ray emission spectroscopy could be applied to wet samples at low energies for the first time with such a source. These methods can provide important information about the electronic and chemical structure of mineral surfaces, but they are difficult to apply under wet conditions unless very high flux and brightness are available in this critical energy region that contains the K edges of the most abundant elements in the environment.

2.3.3.4 Characterization of Surface Complexes and Aqueous Solution Structure at the Mineral/Water Interface.

X-ray standing-wave (XSW) studies and grazing-incidence XAFS methods have not been employed extensively at lower energies, primarily because of flux and brightness limitations at existing synchrotron sources. However, both techniques can provide information about the structure and composition of the near-surface water layer on mineral surfaces, and they are especially important for the elements sodium, aluminum, silicon, chlorine, sulfur, and potassium in natural systems. Grazing-incidence XAFS may be particularly favored because there is much less Bragg scattering and diffuse scattering from substrates than occurs at higher x-ray energies. XSW methods will be able to use larger d-spacing Bragg reflections with larger structure factors at higher incidence angles, also a considerable advantage for probing the electrical double layer at solid-aqueous solution interfaces. Such studies in the energy range from several hundred eV to about 4 keV would be extremely well suited to an undulator source. At the ALS such sources might be used without mirrors, hence avoiding mirror absorption interferences from gold or platinum, which are commonly used coatings. Other complementary techniques that would be useful in determining water structure in this regime are x-ray photoelectron diffraction and holography techniques.

2.4 Actinide Environmental Chemistry

(David Clark and Norman Edelstein, Co-Chairs)

2.4.1 Introduction

The chemistry and physics of actinides are unique in many ways. For example, plutonium exhibits the most complex physico-chemical behavior of any of the known elements. Plutonium metal, for example, exhibits seven allotropic modifications. In some modifications, the 5f electrons are delocalized (itinerant) and bonding, and in other modifications, the 5f electrons are localized (magnetic).

The solution chemistry is equally as rich and complex. The redox potentials that couple the various oxidation states are all remarkably similar at approximately one volt. In addition to the similarity of redox potentials, the tendency of Pu(V) and Pu(VI) to disproportionate, and the slow rate of reactions involving the making and breaking of Pu=O bonds, it is possible for four oxidation states (III, IV, V, VI) to co-exist with one another in appreciable concentrations in the same solution. These factors make the study of fundamental actinide science both difficult and challenging.

The study of actinide chemical and materials properties has recently emerged as an important new area of clear national importance to the environment and to future energy and defense needs, and a relatively large scientific community is currently involved in basic and applied science centered on actinide materials. Many of these researchers are only now realizing the enormous potential of synchrotron-based techniques in solving fundamental and applied problems in actinide science. For example, tunable-energy photons available from modern synchrotron sources provide the capability for a variety of non-destructive experiments on non-crystalline and relatively small samples. The impact of synchrotron-based experiments is now beginning to be recognized within the actinide community, and it is expected to increase significantly over the next several years. Synchrotron-based research is anticipated to have an important impact in areas such as decontamination/ decommissioning, health/ecology/risk, waste forms, fissile materials and storage, spent nuclear fuel, subsurface characterization, waste characterization, waste treatment and destruction, plutonium stabilization, and cleanup.

The ALS will provide the actinide-science community with a unique and complementary x-ray energy range with which to expand fundamental studies of actinide environmental science. Examples of exciting new research opportunities include (1) actinide speciation through spectroscopic examination (absorption, photoemission, x-ray emission) of the actinides themselves and the low-Z elements associated with ligands and substrates (boron, carbon, nitrogen, oxygen, etc.), (2) probing actinide M, N, and O absorption edges where f-electron final states can be observed, (3) the development of new theoretical tools to advance our understanding of the role of f-electrons in actinide materials, (4) actinide surface-science studies to probe the interaction of water and other gaseous molecules with actinide metals and metal oxides, (5) the ability to probe small quantities of radioactive materials due to the high brightness and implementation of spectromicroscopic techniques, and (6) the capability to examine "wet" actinide interfaces in the VUV/soft x-ray spectral region.

2.4.2 Scientific Challenges

2.4.2.1 Surface Chemistry of Actinides

The state of the art in understanding the chemical and structural properties of the surfaces of actinide materials is lagging substantially behind that of other materials systems. Because of radiological safety concerns, the actinide surface-science community has never been able to take advantage of the synchrotron-radiation methodologies in the VUV and soft x-ray regions that revolutionized the approach to surface chemistry and physics over a decade ago. These concerns arise from the difficulty of safely handling, preparing, and performing measurements on actinide surfaces and materials at a soft x-ray/VUV synchrotron-radiation user facility. There have been more than three workshops within the last decade that have specifically addressed the need of the actinide-science community to utilize spectroscopic techniques unique to the soft x-ray/VUV region. Traditional ultrahigh-vacuum (UHV) synchrotron-radiation surface-science experiments need to be performed to understand the surface structures of nominally clean actinide surfaces and to characterize the chemical interactions of small molecules with the surfaces of actinide materials. This knowledge is important to a variety of

actinide-science areas, since advancing the basic understanding of actinide-interface reactions in well-controlled systems directly benefits efforts by those studying processes at complex actinide environmental interfaces. These types of studies span the areas of actinide aging and corrosion, fundamental gas-solid interactions, and fundamental liquid-solid interactions. Specific surfaces of interest include various forms of uranium and plutonium metal allotropes and their corresponding oxide surfaces. Surface chemical reactions of interest include oxygen, water, hydrogen, nitrogen, carbon monoxide, and other small-molecule interactions.

The brightness and flux of the ALS permit the use of actinide microsamples, thereby lessening the radiological risk of handling these materials to an acceptable level. Furthermore, the spectral attributes of the ALS coupled with existing end-station capabilities yield results such as those shown in Figure 3 for actinide microsamples. Specific techniques unique to the soft x-ray/VUV photon-energy region that would be used to investigate actinide surface science will include valence-band and shallow-core-level photoemission, photoelectron diffraction, NEXAFS, soft x-ray emission, and x-ray fluorescence holography. Of particular interest is utilization of soft x-ray emission techniques that are amenable to studies of wet, buried, and poorly prepared actinide materials. Sample requirements include the capabilities to handle larger amounts of actinides to facilitate the preparation of clean, well-characterized surfaces in a UHV environment. In the case of metal or metal-oxide samples, this may require handling up to one gram of non-dispersible material.

Scientific opportunities at the ALS would significantly advance or revolutionize the fundamental knowledge of actinide surface chemistry. Furthermore, these actinide surface-science efforts will also support science-driven programmatic efforts within DOE, including non-proliferation, long- and short-term storage and disposition of nuclear materials, and science-based stockpile stewardship.

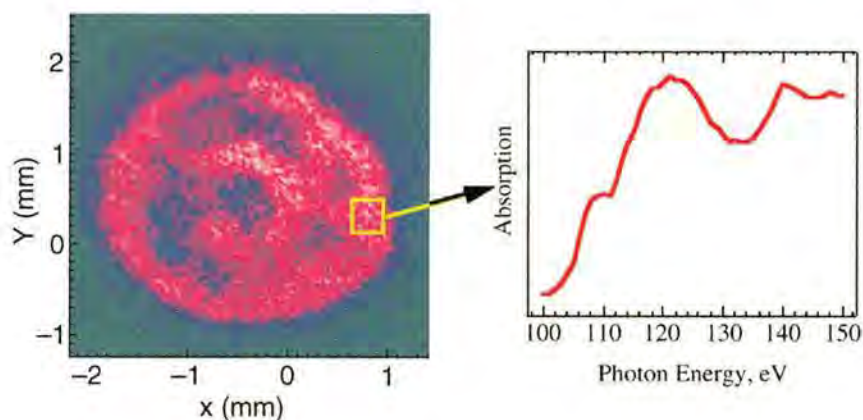


Figure 3. Plutonium (magenta) surface-elemental-concentration map of about 1 microgram of PuO_2 on a platinum (green) substrate obtained from photoemission of plutonium 4f electrons is shown on the left. The right panel is the plutonium near-edge spectrum obtained from the region of the PuO_2 indicated by the box. [Results from ALS Beamline 7.0.1 courtesy of J. J. Bucher, N. M. Edelstein, D. K. Shuh, and E. Rotenberg, LBNL; J. D. Denlinger, University of Michigan; S. D. Kevan, University of Oregon; and B. P. Tønner, University of Wisconsin-Milwaukee.]

2.4.2.2 Transport and Sorption of Actinides

The migration of actinide contaminants in the subsurface will be partially determined by surface interactions between actinide species and the mineral, bacterial, and natural organic surfaces present in the environment. Additionally, anthropogenic complexation may facilitate enhanced transport and affect key surface interactions. A molecular-level understanding of these processes is needed both to predict/model subsurface transport and to design remediation/ immobilization strategies. The ALS can make significant and unique scientific contributions to these molecular-level studies.

There are a wide variety of subsurface environments throughout the complex of sites managed by the DOE where contaminant plumes exist. These include vadose zones in highly silicic iron-rich volcanic ash, groundwater-saturated basaltic rock, deep-subsurface high-salinity groundwaters, and organic-rich near-surface aquifers. Despite this variety, a common theme in the sorption of actinides is the importance and role of metal-oxide minerals. The chemical behavior of actinide/heavy-metal contaminant species in the environment is frequently driven by surface-mediated processes, and it is largely driven by adsorption processes on two types of materials: mineral surfaces, which contain a variety of metal oxides and hydroxides, and colloidal organic matter (COM), which consists of natural humic and fulvic acids and associated compounds.

The ultimate goal here is to understand the fate of the actinides in the environment and the potential risk for contaminant transport from a source term to the far field. This goal is accomplished by understanding the chemical behavior of the solution-borne actinides at the solid-liquid interface. This work also ties in very closely with speciation studies (see Section 2.2) that would in part provide a database of spectral measurements (i.e., core-level binding-energy shifts and valence-molecular-orbital energies) of compounds with actinides in different oxidation states.

There is growing recognition that microbiological interactions play a very important role in defining actinide speciation and mobility in the subsurface. Important interactions include bio-reduction of the multivalent actinides, biosorption, and bio-uptake. Surface complexation of actinide species by microbes, although well established, has not been investigated in detail. This is likely due to the carboxylato, phosphato, sulfato, and nitrogen-based functional groups present on the surface of the microbes in specific geometries. Surface complexation processes may include redox phenomena as well. Soil microbes are typically in the 0.5- μm to 2- μm size range. The key elements for mapping molecular interactions in microbiological systems are ideally situated within the soft x-ray energy range of the ALS. The brightness and flux of the ALS are prerequisites for the spatial resolution needed to distinguish between extracellular and intracellular processes. NEXAFS can be used to provide information on the identity of the actinide element, its oxidation state, and the local coordination sphere about the actinide metal center to identify key details of actinide speciation.

Historically, information about the electronic structure of solid-liquid interfaces has been difficult to obtain. Electron-detection techniques could not be used because of the short attenuation lengths in solution. The capability of performing x-ray emission measurements and XAFS in the total-yield fluorescence mode will allow the study of the electronic structure of these interfaces. By utilizing this technique in the soft x-ray region, both the oxidation state of the actinide and the oxidation states of the light elements in the ligands can be determined. This information cannot be directly observed in the hard x-ray regime.

Experimentally these measurements would be made initially by studying sorption of actinide ions and compounds onto homogeneous, well-understood, and well-characterized planar surfaces of metal oxides and oxyhydroxides of mineralogical interest. These include silicon, aluminum, and

iron-oxide and iron-oxyhydroxide materials. Sorption involves a variety of actinide oxidation states and chemical compounds of interest (carbonates, nitrates, etc.). Chemical interactions of actinides with COM is relevant because of the potential for strong complexation by various functional groups on these materials and their presence in environmental ground water. These experiments may be performed as an actinide/COM binary system or as an actinide/COM/mineral-surface ternary system. Finally, adsorption experiments onto real, heterogeneous, mineral surfaces are required to tie the fundamental investigations to the appropriate environmental situation.

Key advantages and features of the ALS in this general research area include:

- Spectral resolution for speciation studies.
- High spatial resolution for imaging/microscopy of real heterogeneous mineral surfaces.
- Focused beam to investigate small samples (radiological materials).
- Low-energy photons for valence-band and shallow-core-level photoemission.

2.4.2.3 Speciation of Actinides/Heavy Metals

Speciation was identified in the Airlie Workshop Report [1] as one of the most important factors influencing the behavior of contaminants in complex environmental systems. Depending on the system of interest, there are various degrees of detail to which the system has to be defined. Elements of speciation include (1) the identity of the element, (2) the physical state, (3) the oxidation state, (4) the empirical formula, and (5) the detailed molecular structure.

A wide variety of techniques were listed in the Airlie Workshop Report along with the approximate sensitivity limits. Synchrotron techniques were discussed, and it was pointed out that XAFS spectroscopy and variable-wavelength x-ray diffraction techniques provide unique information not available from the usual laboratory-based methods. The ALS provides unique capabilities for studying actinide materials in the soft x-ray/VUV energy region because the small beam size and high brightness allow the use of radioactive microsamples and make it possible to measure directly both the metal ion (M, N, and O edges) and the ligands (K edges), including ligands containing low-Z elements, such as carbon, nitrogen, oxygen, fluorine, and sulfur. An important need is the development of experimental end stations so that radioactive and "wet" samples can be measured with photons in the energy range from 50 eV to 1500 eV to obtain detailed information on "real" samples.

2.4.2.4 Waste Forms

The long-term stability and durability of waste forms for radionuclide disposal are being addressed in repository and actinide-stabilization programs. The general types of waste-form matrices being considered are glasses, ceramics, cements, and the as-is storage of spent nuclear uranium-oxide fuel. Durability issues are centered on surface oxidation and corrosion, stress due to both lattice defects and radiation damage, and solubility of the various phases. Thus, the waste-form materials-science community is a natural candidate to utilize the spatial and spectral resolution of the ALS. This is especially true since many of the important interacting constituents of waste forms can be investigated by XAFS at the K edge (boron, oxygen, alkali metals, aluminum, and silicon) only in the energy regime for which the ALS is optimized. Currently, many of the structural issues in waste-form glasses with these low-Z elements are investigated by nuclear magnetic resonance (NMR) of surrogate materials. However, the capability of the ALS to study small samples will permit the investigation of "real" waste forms containing radioactive material.

In many respects, the scientific issues in this topical area are similar to those being addressed in the areas of speciation and surface chemistry. Molecular-level interactions centered on waste form constituents such as the actinides (M, N, and O thresholds), alkali metals, boron, oxygen, aluminum, and silicon can be studied in the energy range below 2 keV, which is a unique strength of the ALS. Interactions centered on wetted surfaces, near-surface alteration layers that define apparent solubility, and phase identification/characterization in encapsulated and incorporated actinide phases are key to predicting and understanding the long-term durability of waste forms.

2.4.2.5 Fundamental Electronic and Magnetic Structure of Actinides

The major question in actinide chemistry and physics is the nature of the 5f orbitals and their role in chemical bonding. For example, in the light actinide metals and metallic compounds, the 5f orbitals are extended, and 5f electrons display delocalized (band-like) properties. In the heavier actinide metals and metallic compounds, the 5f orbitals are contracted, and 5f electrons are localized into discrete bonds. Heavy-fermion materials are the most dramatic and exciting example of the variety of 5f-electron behavior. The f electrons in these materials are localized at room temperature but exhibit an enormous effective mass as they are cooled, and they can even become superconducting at low temperature. To date, this phenomenon has been mainly limited to cerium and uranium compounds, but it should exist in heavier actinides. Variable-energy resonant-photoemission studies of these materials should provide detailed information about their electronic structure. Theoretical efforts to describe the transition region between localized and itinerant configurations and the formation of quasiparticles responsible for heavy-fermion behavior are also needed. Other fundamental problems that can be examined both experimentally and theoretically in heavy-element research include quantification of material properties arising from the influence of relativistic effects, as well as unusual magnetism in systems exhibiting large orbital moments. Fundamental understanding in these areas will provide insight into the chemical behavior of a wide range of materials, not just the actinides.

(1) Soft x-ray/VUV absorption fine structure (XAFS)

The energy position and detailed features of the x-ray absorption edge contain electronic and structural information about the absorbing ion. Because of safety issues, sample size, and availability restrictions, synchrotron-based x-ray absorption methods often provide information not obtainable by other techniques. Information about the oxidation state, nature of the bonding, and local site symmetry are contained within the edge region. Until recently, this information has been largely qualitative. Recent theoretical efforts have begun to change this picture. Modeling approaches involving scattering to continuum final states are beginning to provide a more quantitative picture of near-edge structure. For example, energy positions of the actinide L edges (17 keV to 24 keV) are currently being used to estimate the oxidation state(s) of the actinide ion(s) in complex environments. The structure of the edge resonance can sometimes be used to infer the presence of a trans-dioxo ion. These data are often augmented by data in the extended (EXAFS) region of the absorption spectrum.

Whereas XAFS at the L edges has become a rather routine tool for probing actinide-ion speciation, the potential of the low-energy actinide edges remains relatively untapped, in part because of the lack of a high-intensity, bright, tunable source of photons in the region of interest (80 eV to 5000 eV). The ALS provides photons in exactly this energy region with extreme brightness, which permits the use of safe amounts of radionuclides, thereby allowing access to these transitions. Their importance is understandable when it is realized that the M, N and O_{4,5} edges involve transitions to the valence f

states. It should be possible to extract much more detailed information about the metal-ion environment, bonding, and electronic structure from these edges. Therefore, XAFS spectra at these edges may provide invaluable and unique information about the electronic structure and bonding of actinide ions. Unfortunately, this information cannot be extracted from higher energy edges using the same theoretical procedures that have proven successful for the K and L edges, because these final states are localized, and modeling approaches that are based only on scattering into continuum final states are expected to provide only part of the picture. However, by bringing to bear known electronic-structure information about actinide ions in well-defined environments, already quantified to some extent by the atomic-spectroscopy community, it will be possible to model the electronic contributions to these near-edge spectra. By combining the experimental and modeling expertise of the synchrotron community with the modeling procedures developed by the atomic-spectroscopy community, this problem could be overcome. Two major research groups will be affected by this effort. The first is the actinide- and environmental-science community, where more detailed information about structure and bonding would help to further understand complexation and reactivity of these environmentally important elements. Information of this type has already proven invaluable to transition metal and main group chemistry. The second is the XAFS community. The electronic contribution to near-edge spectra is not well understood currently. By taking advantage of the simplifications to this problem provided by the lower energy absorption-edge data, it should be possible to extend the information content of this emerging spectroscopy.

(2) Resonant magnetic diffraction

The cooperative magnetic behavior of actinide materials is difficult to quantify. Standard procedures, involving neutron diffraction, are vitiated by the small sample sizes available for experiments. Thompson scattering involves scattering of x rays from electron charges, and therefore is insensitive to magnetic moments. Recently, it has been discovered that when the x-ray energy is tuned near an absorption edge, the standard Thompson scattering is enhanced by second-order effects. Diffraction from magnetically ordered spins can be enhanced by as much as a factor of 10^7 for actinide samples when the x-ray energy is tuned to the M edges. Under favorable conditions, the magnetic-scattering contribution to the diffraction profile is comparable to the charge scattering. Although the details of resonant scattering are not yet fully understood, the potential of this technique for providing heretofore unavailable information about magnetic ordering in a variety of compounds germane to environmental stewardship issues is clear. The magnetic behavior of materials such as plutonium alloys are intimately tied in with the details of their electronic structure. The elucidation and prediction of electronic structure in these materials are necessary for predicting materials behavior over the longer term.

2.4.3 Actinide-Safety Considerations

Working with radioactive materials requires the development of sample-management procedures and safety protocols at the beamline facility where radioactive samples are being run. For many of the soft x-ray/VUV studies, this will require a specialized end station in addition to the one that is currently being constructed at the ALS for electron spectroscopy of the actinides. There will also be the need for radiological monitoring, emergency procedures, and special sample-transport and handling protocols. For example, actinide work might employ an air-exhaust system that has continuous air monitors (CAMS) that can be accessed remotely. The set-up, calibration, and maintenance of these monitors must be carried out by appropriately trained personnel. The protocols for performing experiments with radioactive materials require intensive participation from radiological-safety personnel.

2.5 Microorganisms, Organic Contaminants, and Plant-Metal Interactions

(Brian Tonner and Sam Traina, Co-Chairs)

Biological processes and transformations profoundly influence the fate and impact of inorganic and organic contaminants in the natural environment. These processes are inherently complex in that they involve multiple species and phases, as well as a wide range of spatial domains. Fundamental questions remain on the effects and mechanisms of microbial-mineral interactions, microbially mediated redox reactions, plant and microbial uptake of contaminant metals and trace elements, reactions of organic contaminants and natural biomolecules with mineral surfaces, and the role of mineral systems in the origin of life. All of these problems require spatially resolved information and chemical speciation across a range of spatial scales.

2.5.1 Microbial-Mineral Interactions

Many of the reactive surfaces in these environments are coated with microorganisms and/or biomolecules exuded by plants and microorganisms. These interactions can fundamentally influence the interactions of reactive surfaces with aqueous solutions and with polar and nonpolar solutes. Blocking of mineral surface sites by microorganisms or exuded biomolecules may decrease uptake of metals and oxoanions by metal oxides and clay minerals. Additionally, the biosurfaces represented by microorganisms, tissues, and extracellular biomolecules can provide sites that compete with inorganic sites for uptake of dissolved metal ions or participate in ternary complexes comprised of minerals, metals, and organic functional groups. Molecular-level information on these important systems is presently lacking. In particular, information is needed on the local speciation and surface-coordination environments of metals on microbial and plant surfaces, as well as within subcellular structures. Biogeochemically induced changes in metal oxidation states have been observed at the cellular and subcellular level of microorganisms and plants. However the current scale of spatial resolution available is inadequate to fully understand the local chemical environments within and on subcellular organelles that are responsible for observed macroscopic changes in metal concentrations and metal oxidation states. *In vivo* NEXAFS spectromicroscopy on the scale of 0.1 μm (K-, L- and M-edge spectra of metals and carbon, sulfur, nitrogen, and phosphorus K-edge spectra of metal binding sites) will facilitate a much greater understanding of the biogeochemical speciation of metals in natural environments.

Microorganisms also play an important role in the formation of many minerals. Many of the reactive minerals in soils and sediments are of biogenic origin, and microorganisms participate in the formation of precipitates of these solids (metal oxides, carbonates, phosphates, sulfides, etc.). These biogenic phases can significantly alter the solubility and transport of many contaminants in natural systems. For example, the formation of plutonium phosphates by soil microorganisms can potentially decrease the concentrations of dissolved plutonium in groundwater, thus diminishing plutonium transport. These are particularly challenging systems to investigate because the reaction products are often of nanoscale dimensions, with only short-range order and variable chemical composition. Our current state of knowledge is limited by *ex-situ* studies of these systems, which potentially introduce artifacts associated with sample preparation. Additionally, questions remain on the exact composition of these biogenic materials. Conventional microscopic methods can provide information on trace-metal composition, but data on the inclusion of biomolecules are lacking. Yet, it can be anticipated that close association of these solids with microorganisms may result in the incorporation of low-molecular-weight organic acids within the solid matrices. Such possibilities beg for spatially resolved,

spectral information on the contents and speciation of both organic and inorganic components within these materials. With such information, it will be difficult, but possible, to predict their thermodynamic solubilities and long-term stabilities. Lacking this information, such predictions are not possible.

2.5.2 Microbially Induced Redox Environments

The metabolic activities of microorganisms have been postulated to cause the formation of micro-redox environments with local oxidation-reduction potentials much different from that of the bulk solution or the surrounding porous media. The spatial scale of these effects is thought to range from nanometers to millimeters. The former should occur at the buried interfaces between microorganisms and mineral surfaces, while the latter may span from the interior to the exterior of a soil aggregate. These microscopic redox environments could cause important changes in the oxidation state and chemical mobility of important metals and anions that cannot be predicted from the macroscopic redox state of the bulk-soil or sedimentary environment. Unfortunately, direct information on these redox gradients is lacking. Spatially resolved spectromicroscopy would allow the determination of local oxidation states in the environments of interest. This has major implications in the distribution of trace elements, as well as larger scale issues, such as the potential for anaerobic microbial processes (e.g., denitrification and microbial methane production) in dominantly aerobic environments. Whereas trace-element distributions are important relative to local-scale problems of contamination, the production of N_2O and CH_4 by soil and sedimentary microorganisms has implications in green-house gas cycles and global change.

2.5.3 Corrosion and Biofilm Formation

Corrosion shortens the life of pipes, ships, and buildings. It is now recognized that many corrosion reactions are mediated by microbes. The onset of these corrosion reactions often involves attachment of microorganisms to the substrate and subsequent biofilm formation. Spectromicroscopy can potentially help us to answer the following questions: what induces the microbes to attach to the surface and are there particular geometries or conditions that the microbes prefer? A better understanding of microbial attachment and biofilm formation would help in the synthesis and design of corrosion-resistant materials and the preservation of archaeological sites. This could result in significant monetary savings for society.

2.5.4 Origin-of-Life Issues

Clay minerals have long been postulated to have served as a template for the origin of life. Organization and polymerization of base pairs on clay surfaces may well have led to the formation of the first oligonucleotides and proteins. Questions remain on the exact nature of the reactions at the clay-water interface. Spatial variability in layer charge and crystal chemistry of individual clay particles precludes a full understanding of these paleo-organic chemical reactions. Noninvasive *in-situ* studies are needed to examine these local-scale effects on interactions of protein precursors with the clay mineral surfaces.

The potential for life on other planets and/or extraterrestrial origins of life on Earth have recently received greater attention, owing to the reported discovery of extraterrestrial biomolecules in Martian meteorites. Admittedly, much controversy remains concerning the origin of these materials. Nevertheless, the possibility of extraterrestrial microscopic life remains an intriguing concept. A definitive assessment of this possibility is perhaps one of the most scientifically and philosophically challenging

issues for humankind today. Careful examination of extra-planetary materials requires highly resolved spectrochemical information on organic molecules and their surrounding mineral matrix to distinguish between substances produced by biotic and abiotic processes. Such information could be provided by x-ray spectromicroscopy, aiding us in our quest to understand the origin of life.

2.5.5 The Interactions of Plants with Heavy Metals and Trace Elements

The uptake and biochemical transformation of heavy metals and trace elements by plants has long been an area of study in the fields of plant physiology and agriculture. Much of this effort has been driven by the desire to increase production of food and fiber. Recently, considerable attention has focused on the use of plants as extraction systems for the removal of pollutants from soils and aquatic systems. When applied to soils, this process begins with growing plants that can hyperaccumulate toxic elements in their tissues and finishes with harvesting these plants to remove the toxins from the contaminated site. Some hyperaccumulating plants may also transform a toxic species into a less toxic form or produce a volatile species of the toxic element. This field, known as phytoremediation, faces several pressing scientific challenges. Perhaps the greatest of these is determination of the specific loci and chemical composition of metal binding sites within the plant materials. Higher plants are complex multi-cellular organisms with molecular structures that vary in composition at the single-cell and organ levels. Information is needed on the temporal and spatial variations, as well as compositional variations of metal-binding proteins within these organisms. Unfortunately, many of these are located in subsurface structures (roots). Thus, metal-accumulating plants grown in metal-contaminated soils often lead to the accumulation of metals in the roots and not in the above-ground biomass that can be more easily harvested and removed off site. Specific chemical information is needed on the nature of the metal-binding sites within hyperaccumulating plants. Namely, information on the local chemical speciation of the trace elements within the plants as well as the chemical structures of the metal binding proteins must be obtained to develop a comprehensive understanding of this phenomena. Coupling this information with plant-molecular biology methods may lead to better and more efficient metal accumulating plants, ultimately, facilitating timely treatment and cleanup of toxic environments.

3. General Conclusions and Recommendations

Several major conclusions and recommendation can be derived from the information provided above and from the results of two past workshops devoted to synchrotron-based molecular environmental science [1,2]:

3.1 Conclusions

1. Synchrotron-based methods, particularly XAFS, microXAFS, soft x-ray/VUV spectromicroscopy, and photoemission methods, are having a major impact on MES and the earth sciences by providing unparalleled information on molecular speciation of elements ranging from boron to plutonium at unprecedented spatial scales (nanometers to millimeters) in complex multiphase materials. Such methods are also providing unique molecular-scale information on important chemical processes relevant to these fields, including those occurring at environmental interfaces, in plants, and in microorganisms.

2. Although there will soon be an adequate number of hard x-ray beam stations devoted to or available for MES research (estimated to be about 8 full-time equivalent beam stations by 1999), which

should satisfy the needs of this community for the next three years, according to a national user survey [1,2], there is no soft x-ray/VUV beam station optimized for and dedicated to MES research at any of the DOE synchrotron light sources.

3. Technical support of MES and earth-science users at the ALS is currently inadequate, which means that only a few experienced users can effectively utilize the unique capabilities of the ALS in the soft x-ray/VUV energy region.

4. Because of the growing need for routine XAFS and microXAFS analyses of large numbers of environmental samples, it is important for the DOE to consider the development of several beam stations, including both hard x-ray and soft x-ray/VUV stations, at DOE synchrotron light sources that would be devoted to routine analytical work involving XAFS and micro-XAFS spectroscopy. Adequate staffing of these beam stations is an important issue that might be best handled by a small business that would provide an analytical service. Without these types of facilities, it is unlikely that synchrotron-based studies of environmental samples will have a major impact on environmental decision making. It is apparent to the members of this working group that information on chemical speciation in environmental samples could result in enormous cost savings to the U.S. government, as well as private citizens, through improved and more cost-efficient remediation technologies.

5. Based on joint discussions of the Working Groups on the Environmental and Earth Sciences and on New Directions in Surface Science at the ALS Workshop, there is significant scientific and intellectual overlap between these two groups, particularly in the area of surface and interfacial chemical processes, and a need for similar specialized experimental facilities at the ALS. Development of compatible facilities required by these two communities will also lead to desirable collaborations among scientists in these complementary disciplines.

3.2 Recommendations

1. This working group strongly recommends that a beamline be designed and built at the ALS that would operate in the 800 eV to 4,000 eV range and would be equipped with appropriate optics to provide spot sizes in the submicron range for microXAFS applications. The extreme brightness of the ALS in this energy region would result in unique microspectroscopy capabilities for many of the low-Z elements that comprise the bulk of the Earth's near-surface environment. This capability could also be extended to the L edges of the first-row transition metals and the M and N edges of the actinide elements, which are extremely important in an environmental context. Such a beamline would help satisfy one of the most important needs in MES research—quantitative information on the spatial distribution at the submicron scale of the different chemical forms of metal ions in complex environmental samples.

2. This working group also strongly recommends that a beamline designed for spectromicroscopy studies in the VUV energy region (50 eV to 800 eV) be developed at the ALS and optimized for MES applications, including the study of wet samples using differentially pumped sample cells. Innovative research in this area at the ALS is already providing some of the first molecular-scale, chemically specific information on functional groups on humic and fulvic substances, which are ubiquitous high-molecular-weight organic compounds in the environment and are responsible for the sequestering and transformation of many heavy metals. However, the current level of beam time for these types of projects at the ALS is so restricted that little work can be accomplished each year.

3. X-ray emission spectroscopy is a venerable technique that has been explored to new depths at the ALS and has great potential for providing unique information on the bonding of adsorbates at

environmental interfaces, including solid-water interfaces [4]. We strongly recommend that the ALS management devote adequate resources to rebuild the unique x-ray emission capability that was previously provided by the loan of equipment by the University of Uppsala and the expertise of Dr. Anders Nilsson.

4. A concerted effort should be made to increase the level of technical support provided by the ALS to the user community in general and the MES community in particular. This is especially important in the soft x-ray/VUV area where the technical difficulties associated with a UHV experiment are often greater than those in the hard x-ray region, which do not generally require UHV systems.

5. To help stimulate cooperation among the four DOE synchrotron-radiation laboratories in the area of MES research, as well as among individual researchers, this working group recommends that MES beam-station facilities at the various labs be standardized as much as possible so that samples can be transferred from one beam station to another among the facilities for spectroscopic, spectromicroscopic, and diffraction studies on the same portions of a sample using beamlines operating at different energies. A standardized sample stage, with appropriate fiducial marks, and standardized sample holder available at different MES facilities at the four labs would greatly facilitate such studies.

6. The MES effort in the U.S. involves a growing community of users working at all four DOE-supported synchrotron-radiation laboratories. It is essential that future developments of MES beamlines and beam-station experimental facilities supported by DOE funding be based on community needs and community input. In order to help stimulate cooperation among MES users at the ALS, APS, NSLS, and SSRL and to further develop the MES community nationally, an ENVIROSYNC organization should be formed. This organization should meet annually to assess the synchrotron needs of the MES community and to develop a roadmap for future facilities developments.

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Working Group on Biosciences

Chair: Graham Fleming, University of California, Berkeley

1. Overview of the Biosciences

Research in the biological sciences at the ALS has undergone explosive growth in the past year, with the percentage of users rising from about 4% to about 20% in the period from September 1997 to March 1998. This increase is due in large part to the onset of operation of the Macromolecular Crystallography Facility (MCF), which is using Beamline 5.0.2 at the ALS, as a national user facility for biological crystallography (see Section 2 below), but also to recent scientific breakthroughs using x-ray microscopy to localize subcellular entities at Beamline 6.1.2.

Bioscience research at the ALS is concentrated into three areas: crystallography, microscopy, and spectroscopy. These fields form a set of complementary approaches to study living organisms from the molecular to the cellular levels. Crystallography is used to determine the atomic-resolution, three-dimensional structures of proteins and nucleic acids—the building blocks of life—as well as complexes of these molecules, the interactions of which give rise to biological processes. Microscopy allows us to find the where these biomolecules are localized in the cell and visualize the cell's overall organization. Spectroscopy yields information on the chemistry of these molecules, especially the chemistry of metalloproteins that act as enzymes.

Following the division of bioscience research at the ALS, the Working Group on Biosciences comprised three sub-groups: Protein Crystallography, Soft X-Ray Microscopy, and Biological and Chemical X-Ray Spectroscopy. Here we present separate reports for each of the sub-groups.

2. Protein Crystallography

Facilitator: Thomas Earnest, Lawrence Berkeley National Laboratory

Working-group members: Tom Alber, University of California Berkeley; Kristin Balder-Froid, Lawrence Berkeley National Laboratory; Rich Bott, Genencor International; John Byrd, Lawrence Berkeley National Laboratory; William Chang, ARACOR; Kenneth Downing, Lawrence Berkeley National Laboratory; Ulrich Genick, The Scripps Research Institute; Bob Glaeser, University of California Berkeley; Todd Hansen, Lawrence Berkeley National Laboratory; Michael Hart, Brookhaven National Laboratory; Keith Henderson, Lawrence Berkeley National Laboratory; Keith Hodgson, Stanford University; Li-Wei Hung, Lawrence Berkeley National Laboratory; Alan Jackson, Lawrence Berkeley National Laboratory; Sung-

Hou Kim, University of California Berkeley; Thomas LeBrun, National Institute of Standards and Technology; Gerry McDermott, Lawrence Berkeley National Laboratory; Wladek Minor, University of Virginia; Keith Moffat, University of Chicago; Harry Noller, University of California Santa Cruz; Hans Parge, Agouron Pharmaceuticals, Inc.; Georgeanna Perdue, Lawrence Berkeley National Laboratory; David Robin, Lawrence Berkeley National Laboratory; Bernard Santarsiero, University of California Berkeley; Ray Stevens University of California Berkeley; Bob Stroud, University of California San Francisco; Edwin Westbrook, Argonne National Laboratory.

2.1 Opportunities in Protein Crystallography

In many respects, protein crystallography is a mature but constantly evolving field. Exciting biology is being done daily by the application of x-ray crystallography to determine macromolecular structures. At the same time, crystallography has its own scientific frontiers. The sub-group on Protein Crystallography pointed to five in particular.

2.1.1 Structure Determination at Very High Resolution

As improvements in molecular biology, purification, and crystallization take place, there has been an increase in the number of protein structures that can be solved to ultrahigh resolution (better than 1.0 Å). Higher resolution results in a more accurate determination of atomic positions, thus leading to an increased understanding of the molecular mechanisms of enzyme catalysis, ligand binding, etc. In some cases, hydrogen atoms, which are important in the many catalytic mechanisms, can be seen. Obtaining higher resolution also means that more experimental data are available by means of the increased number of reflections present, therefore improving the crystallographic-refinement capabilities by increasing the observations-to-parameters ratio. Also, direct methods can be used to solve the phase problem in some cases if adequately high resolution is obtained.

2.1.2 Structure Determination from Microcrystals

The successful routine determination of structures from microcrystals would dramatically increase the number of macromolecules available for crystallographic study. Membrane proteins are a classic example of molecules difficult to crystallize; they are likely to be available (if at all) only as very small crystals. Microcrystals are also the likely first products of proposed robotic systems for protein crystallization. The data from microcrystals can only be collected with the use of synchrotron-radiation sources.

2.1.3 Studies of Large Macromolecular Complexes

Prominent examples of macromolecular complexes include ribosomes and multiprotein or protein/nucleic-acid complexes. Such complexes often represent the most fascinating frontiers of cell biology. Notably, such complexes will not generally be revealed by structural-genomics projects (about which, more later), which will likely deal with individual proteins, separately expressed and crystallized. It is in the specific interactions of biomolecules that biological processes are activated and modulated, necessitating the structure determination of these molecules and their complexes for a complete understanding of these processes at a molecular and cellular level.

2.1.4 Determination of Large Numbers of Structures in Coordinated Projects

Structural-genomics projects propose to characterize a significant fraction of the proteins coded by an entire genome. Such ambitious plans depend absolutely on robotic expression and crystallization, on speedy and accurate data acquisition, and on automated structure determination and refinement. Another example of coordinated projects is iterative structure design, in which rapid feedback of structural information for a

given molecule is used to direct subsequent structural modifications as part of, say, pharmaceutical development, and to influence the priorities with which subsequent structures are examined.

2.1.5 Time-Resolved and Other Mechanistic Studies

Time-resolved studies currently span time scales from minutes to nanoseconds, but efforts are under way to push into the sub-picosecond regime. However, these advances will require substantial ancillary equipment, including fast shutters, laser systems, and single-crystal microspectrophotometers. Other examples of mechanistic studies include coordinated studies of hundreds of protein variants, studies of complexes with hundreds of ligands, investigations at a range of pH values, and studies of freeze-trapped intermediates.

2.2 Current and Future Needs

To address these opportunities, as well as the more routine needs of structure determination, it is natural to ask whether current facilities are adequate. The demand for crystallographic facilities is growing so rapidly that current needs may be an unreliable guide to the scale of facilities required over the next three to five years. As a starting point, however, it is necessary to clearly define the current level of demand. Therefore, the sub-group focused its attention on the West Coast. As indicated in the boxed sidebar, available beam time at West Coast facilities appears to be well matched to the *present* needs of “local” crystallographers.

This conclusion may already be inaccurate, however, as several working group members reported significant “oversubscription” of operating beamlines. This additional demand arises in part from a “latent” group of users. In addition to the needs of established, dedicated crystallographers on the West Coast, demand is increasing among protein biochemists who are now growing crystals in their own laboratories. These users typically possess great insight into medical and scientific issues, and involving them directly in the process of structure determination can promote a highly desirable synergy between biochemistry and structural biology. It will also surely reduce the time that elapses between the identification of an interesting target protein and the use of that structural information to drive new biochemical experiments. Involving protein biochemists early on will also ensure that protein samples are crystallized in the most desirable biochemical states (e.g., phosphorylation state, oxidation state, degree of glycosilation). It is also interesting to note that many of the proteins that are medically most interesting do not pose significant hurdles for structure determination. Many are soluble and fall into the size range that is easily accessible with current techniques.

The number of principle investigators (PIs) who fall in this “latent” category is difficult to estimate. But from an informal survey at an institution represented by a member of the sub-group, the number of protein biochemists interested in protein structure determination by x-ray diffraction was conservatively estimated to be three times that of crystallographers per se. At the same time, the number of projects within these labs is typically limited to one or two at a time. Accounting for the beam time required by this user group would at least double the beam time estimates based on the core of West Coast protein-crystallography groups.

The opportunities presented in Section 2.1 suggest a qualitative change in the way protein crystallography will be carried out in the future. We cite three examples in particular which will require dramatic increases in the resources now available: (1) structural genomics, such as the *Methanococcus jannaschii* project described later in this report, (2) iterative structure-based drug design, and (3) large molecular complexes, such as the ribosome.

Current Demand for Beam Time

About 80 principal investigators pursued macromolecular crystallography in 1997–98 on the West Coast (defined as extending east to the Rocky Mountain states and Texas and including Alberta and British Columbia)—a number that encompasses industry, academia, and government. (We assume that the use of other U.S. facilities by West Coast crystallographers is balanced by the influx of other crystallographers to West Coast facilities.) To project current needs, we made three assumptions:

1. Each PI has an average of five projects active at all times. A range from two to fifteen is likely, with a peak in the range of three to six; only a very few labs have more than eight active projects.
2. Each structural project requires an average of ten data sets (three or four are actually the minimum for *de-novo* structure determinations). Certain structural sub-projects require only one good data set (e.g., a single protein-ligand complex); other projects may require 1000 data sets.
3. Each data set requires an average of 100 images (more if fine ϕ -slicing is used and if 180° of data are required) or about 12 hours of scheduled beam time. We take 1000 images to be the maximum (e.g., 180° at 0.2° intervals) and about 20 the minimum (e.g., 60° range with 3° oscillations).

The typical facility runs 5000 hours per year—about 220 scheduled user days. Thus, one station can accommodate about 10 PIs, and for the 80 PIs who are assumed to work exclusively at West Coast synchrotrons, eight stations are needed. In fact, seven stations are currently operational (or soon will be): Beamlines 5.0.2 and 5.0.1 (operational within 18 months) at the ALS, and Beamlines I-5, VII-1, IX-1, IX-2, and XI-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). Consequently, there *presently appears* to be a rough balance between station supply and demand, although there is a backlog of interesting projects at all facilities. This conclusion agrees with the 1997–98 BioSync Report (available at www.ornl.gov/hgmis/biosynch).

2.3 The Advanced Light Source: Successes and Opportunities

2.3.1 The Macromolecular Crystallography Facility

Beamline 5.0.2, the first beamline of the ALS Macromolecular Crystallography Facility (MCF), collected its first diffraction patterns from protein crystals on 18 September 1997. Optimized for multiwavelength anomalous dispersion (MAD) experiments, the MCF was initially used to record several data sets from test crystals. These tests, conducted on lysozyme and on a platinum derivative of lysozyme, gave excellent statistics (values of R_{symm} from 3.5% to 4%) to a resolution of 1.6 Å, successfully demonstrating the capabilities to collect and process data accurately.

The subsequent initial user run of the MCF was extremely productive, with users from academic, industrial, and national laboratories successfully collecting MAD data, diffraction data from micro-crystals, and “conventional” diffraction data with extremely rapid throughput. In all, over 60 users

from 18 different groups collected data at the MCF between 15 November 1997 and 31 January 1998. User demand has accelerated. As of 12 April, 1998, the number of users had grown to 94. This figure represents 25 different groups from a strong mix of universities, industry, and national laboratories. Current requests for beam time indicate demand will substantially exceed the time available during the upcoming operational period. MAD results included data from ApoE, a protein important in cholesterol metabolism (to 1.8 Å), and from MJ0577, a hypothetical protein from the genome of *M. jannaschii* (to 1.6 Å).

Data from several microcrystals were also collected. In the most dramatic case, scientists from Roche Biosciences collected an entire data set to 1.8-Å resolution from a frozen microcrystal measuring approximately $40 \times 30 \times 5 \mu\text{m}$. The structure of this drug-design target-inhibitor complex has subsequently been determined by the same group. Both the Scripps Research Institute and Genentech have utilized the high-throughput capability of the MCF for rapid data collection. Also, Barry Stoddard's group at the Fred Hutchinson Cancer Research Center collected 1.6-Å data from Ppo-I, an intron-encoded endonuclease having a base-pair specificity of 20, in less than two hours (see Figure 1).

Initial results from the MCF are thus extremely encouraging, fully justifying its description as a world-class facility. Furthermore, an additional order-of-magnitude improvement in brightness is expected when final optics are installed (replacing the current temporary mirrors) and the beamline is fully optimized.

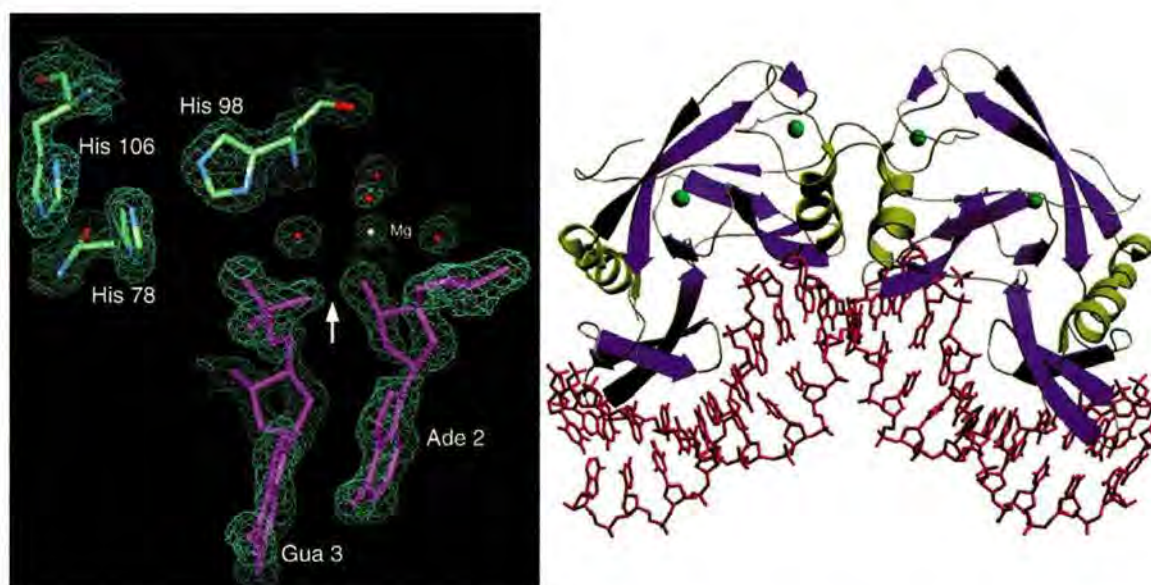


Figure 1. Ppo-I, an intron-encoded endonuclease that recognizes and cleaves 20 base-pair sequences with a high degree of specificity. The structure was solved by Barry Stoddard, Melissa Jurica, and Karen Flick of the Fred Hutchinson Cancer Research Center with data from the Macromolecular Crystallography Facility extending to 1.6-Å resolution. (a) Active site with electron density of Ppo-I. (b) Ppo-I dimer bound to DNA-recognition site. [Figure courtesy of Barry Stoddard, Fred Hutchinson Cancer Center.]

2.3.2 New Opportunities

Within a few short months, the MCF has thus fully confirmed the suitability of the ALS for protein crystallography, raising natural questions about how the most exciting opportunities in the field can be mapped onto the capabilities of this facility. In the course of its discussions, the Protein Crystallography sub-group pointed to six opportunities, each an expression of an exciting opportunity in protein crystallography, judged especially appropriate to the physical capabilities and resident expertise at the ALS.

2.3.2.1 Structural Genomics

In recent years, large-scale sequencing projects have begun to provide gene sequences from a number of organisms and, in some cases, the complete inventory of the organism's genetic information. The first complete sequence was published in 1995, and within two years, ten additional organisms had been completely sequenced. This knowledge will certainly advance our understanding of biology and medicine, especially after the structure and function of the genomic products are determined. To take this next essential step, large-scale structure-determination projects must be combined with the sequencing efforts to look for novel protein-folding patterns, to understand the function of genomic products, and to uncover proteins of previously unknown function. As an important stride in this direction, the fully sequenced microbe, *Methanococcus jannaschii*, is being used in a pilot study for structural-genomics research. Sung-Hou Kim at UC Berkeley and LBNL and his colleagues have chosen several gene products from this organism—some with known homologues and some without—and have begun to determine their structures. Early results from the MCF have already allowed the role of a “hypothetical” protein to be tentatively identified from its structure alone.

2.3.2.2 Iterative Structure-Based Drug Design

The process of drug discovery can be greatly accelerated by knowing the structure of the target molecule, which can allow the design and synthesis of compounds that activate or inhibit the target. This process of rational drug design usually requires an iterative procedure in which trial compounds are designed to fit the active site or ligand-binding region, crystals are obtained of the target-compound complexes, the structures of the complexes are solved and analyzed, and the results then used in the design of the next round of trial compounds. Since many steps and many compounds are needed before yielding a compound with high binding affinity and the needed specificity, several structures need to be solved. This calls for high-throughput crystallography beamlines, which offer both speed and high data quality.

2.3.2.3 Robotic Expression and Crystallization

Expressing, purifying, and crystallizing proteins for crystallography are tremendously demanding of research time and research dollars—far more so than the actual collection and analysis of x-ray data. Crystals are typically grown one at a time, and efforts are made to improve the crystal-growing conditions, one variable at a time. Fortunately, this procedure is ideal for employing the kinds of automated systems recently developed for DNA sequencing, directed evolution, and combinatorial chemistry. By exploiting the high-throughput capabilities of the ALS, an automated approach to protein expression, purification, and especially crystallization has the potential to turn drug design and protein engineering into efficient iterative processes.

2.3.2.4 Membrane Proteins

Although 30% to 40% of the proteins encoded by the genomes of organisms are membrane proteins, fewer than 1% of the structures solved to date fall into this class. There are several reasons for this situation: (1) Membrane proteins exist simultaneously in three distinct environments (extracellular, intracellular, and membrane-embedded), which are difficult to duplicate together in crystallization media; (2) overexpression in heterologous systems rarely produces large quantities of correctly

folded protein, and very few can be purified in adequate quantities from native sources; and (3) once out of the membrane, these proteins are frequently unstable. Further, crystals of membrane proteins usually diffract rather weakly and have large unit-cell parameters. Thus, it is critical for membrane-protein projects to have access to bright synchrotron-radiation beamlines if they are to succeed. During screening, synchrotron radiation is needed to assess the quality of membrane-protein crystals, thus providing guidance in efforts to improve crystallization conditions. And when studying typically small crystals with large unit cells, the ability to achieve a high degree of collimation and a small spot size is necessary for obtaining high-resolution data.

Membrane proteins are responsible for all forms of cell-cell signaling, sensing of external stimuli, and the transport of molecules across the apolar cell membrane. Owing to their biomedical importance, it is critical that synchrotron-radiation resources be dedicated to investigating this challenging family of proteins. The ALS benefits from a large local concentration of researchers with appropriate expertise who might serve as the basis of a scientific program in the structural biology of membrane proteins.

2.3.2.5 Large Molecular Complexes

An accurate and comprehensive understanding of most, if not all, cellular processes requires the atomic-resolution structure determination of the biomolecules involved. Many important biological problems can be understood only in the context of their interactions with other molecules. In this regard, the use of synchrotron radiation has become ubiquitous and vital. The use of synchrotron-based crystallography to determine atomic-resolution structures of large biomolecular complexes—ribosomes, multi-subunit enzymes, transmembrane proteins, DNA-binding assemblies, ligand-receptor complexes—enables an extension of our understanding of molecular and cellular biological processes to the level of atomic resolution. An example is the ribosome, a 2.5 megadalton complex of three RNA molecules and over 50 protein molecules that translates genetic information into the production of proteins. Harry Noller and his colleagues from UC Santa Cruz, working with scientists from the MCF at the ALS, have made progress recently toward solving the structure of this complex. Figure 2 shows the structure of the 70S ribosome at

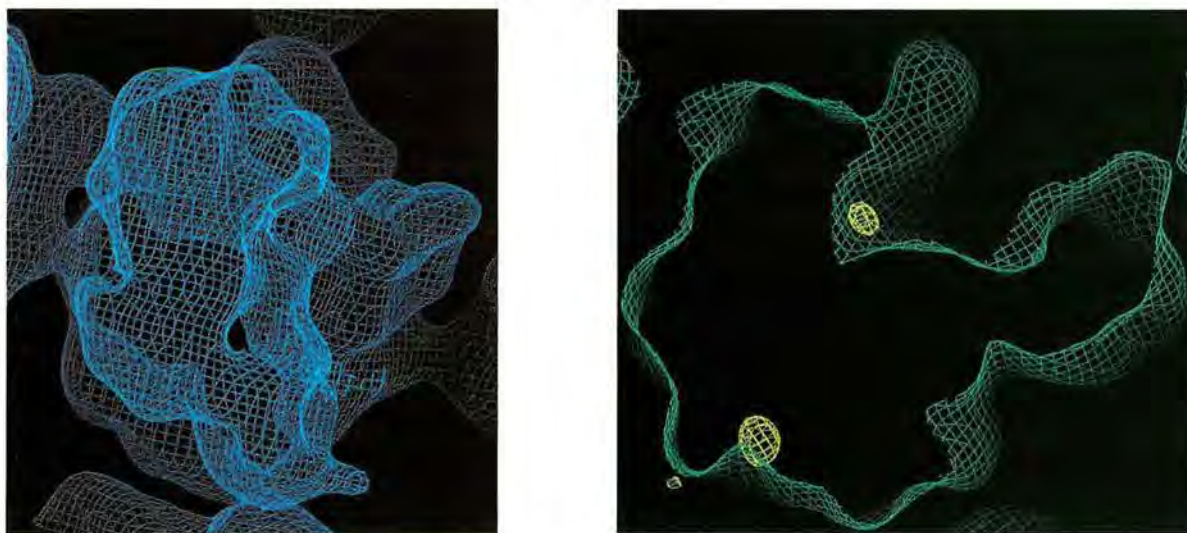


Figure 2. (left) Electron-density map at 30-Å resolution of *T. thermophilus* 70S ribosome contoured at 1σ . (right) A difference Fourier map contoured at 4σ showing two sites from a heavy-atom derivative superimposed on the 30-Å map. Phases for both maps are from a molecular-replacement solution using a cryo-EM model of the *E. coli* 70A ribosome. [Figure courtesy of the Henry Noller group at the University of California, Santa Cruz.]

30-Å resolution, obtained using phases derived from electron microscopy. Such projects as this represent unique opportunities for high-brightness synchrotron sources such as the ALS, which are necessary if one is to see diffraction to even moderate resolution, and tuning the energy allows the use of anomalous-diffraction methods for obtaining phasing information.

2.3.2.6 Low-Energy Diffraction

The ALS is especially well suited to utilize x rays in the 2- keV to 8-keV range to collect anomalous data from elements with absorption edges in this region, including uranium, calcium, potassium, and sulfur. The uranium M_V edge would be especially useful, since the anomalous signal at 3.55 keV is large enough to phase large complexes, such as the ribosome. Experiments at these energies require special end-station instrumentation to minimize absorption and to detect the x-rays scattered at large Bragg angles.

2.4 Recommendations

Considering the opportunities for the broad field of protein crystallography, the needs of its practitioners, and the capabilities of the ALS, the Protein Crystallography sub-group identified five specific scientific thrusts for the future development of the facility.

2.4.1 Complete Beamline 5.0.1

A continuing priority for the ALS should be the completion of Beamline 5.0.1, which should roughly double the facility's current capacity for protein crystallography. Beamline 5.0.1 is under construction as a side station from the wiggler, using an asymmetrically cut, curved-crystal monochromator. The wavelengths available will extend from 0.95 Å to 1.6 Å, and the total flux on the sample will be approximately the same as on beamline 5.0.2. This project is jointly funded by LBNL, Amgen, Roche Biosciences, UC Berkeley, and the Lawrence Livermore National Laboratory. The beamline is scheduled to begin operation in August 1999 and will be utilized for monochromatic-crystallography experiments.

2.4.2 Encourage Structural Genomics Research as a Vital Component of the ALS Scientific Program

A detailed time analysis has shown that extraordinary resources will be required to complete the project of solving the structures of all the proteins from a single microbe, such as *Methanococcus jannaschii*. The need to pursue structural genomics projects for a number of such organisms underscores two pressing imperatives: an increase in the beam time available to these projects and enhanced efficiencies in the expression, purification, and crystallization of the genomic products. The following two recommendations address these two issues.

2.4.3 Add Three Superbends

As part of an research and development program for extension of the capabilities of the ALS across the whole energy spectrum, a program was started more than three years ago aimed at producing superconducting bend magnets (superbends) to replace three of the 36 dipole magnets of the ALS. Each magnet can have up to four beamlines. The field at the tangent points is 5 T and therefore increases the critical energy of the superbend synchrotron radiation by a factor of four over a normal bend magnet. The higher critical energy increases the figure of merit for crystallography performance at 12 keV by a factor of 10. For typical crystals (0.3 mm in size), an ALS superbend beamline will give, for example, 2.9 times the useful flux of SSRL wiggler Beamline IX. Not only will this give the

ALS outstanding high-energy performance, it will do so at a fraction of the cost of a high-power wiggler beamline. The proposed ALS superbend sources will deliver flux densities of at least 6×10^{12} photons/(sec-mm²), which is approximately equal to the most intense x-ray field strength tolerable to protein crystals (see Section 2.5 below). By comparison, more powerful radiation sources at third-generation synchrotrons (undulators and wigglers) must be attenuated to the field strength of the superbends to avoid damaging the sample crystals. The ALS superbends, therefore, are an optimal x-ray source for most protein crystallography projects.

Since the ALS superbend sources are substantially less expensive than insertion-device sources, they are a cost-effective solution for the future needs of protein crystallography. Equally important, the superbend designs permit the expansion of scientific capability without compromising the other core scientific programs of the ALS; namely, soft x-ray and vacuum-ultraviolet (VUV) applications. They do not encroach upon the straight sections of the ALS, which are valued for their insertion-device capability. There is apparently no "down side" to the superbend sources, and their implementation at the ALS will permit this facility to achieve a balanced growth of science in many areas, simultaneously.

2.4.4 Develop a Robotic System for Expression and Crystallization

It is highly appropriate to exploit the advantages of robotics at the ALS to reduce the manpower needed for protein expression, purification, and crystallization and to open the door to high-throughput investigations of protein structure. A system currently being developed will use nanoliter amounts of protein sample per trial, instead of the microliter amounts now needed. This modification will save precious protein material, and the microcrystals that will result can be effectively used on beamlines at the MCF. In addition, optical-screening methods will be used to reduce the current effort involved in examining one crystallization trial at a time and recording observations in a notebook. By storing and analyzing recorded images, this automated system will allow protein crystals to be produced far more efficiently. In addition, by using this resource to screen and analyze large arrays of conditions critical in the crystallization of many proteins, for example membrane proteins, we can expect valuable clues to emerge for the crystallization of these difficult proteins.

2.4.5 Promote the Development of Pixel Detectors

There is a clear need for advanced detectors for protein crystallography. Experience during the past decade in this field has shown that every advance in detector design has yielded improvements in both the quantity and the quality of crystallographic structures determined on synchrotron sources. Implementation of image-plate (IP) detectors and their subsequent development and improvement made possible several stages of extraordinary advance over the previously used x-ray film. More recently, CCD area detectors have been implemented on synchrotron sources, with consequent further enhancements in spatial resolution, speed, and data quality.

The development of silicon pixel-array detectors (PADs), now under way at Berkeley (in collaboration with UC San Diego), is very important for this field. These detectors are based on direct photon counting using a high-density array of silicon photodiodes, directly connected to an application-specific integrated circuit (ASIC). The detectors have a photon-energy operating range of 4 keV to 15 keV, a typical array size of 1000×1000 pixels, a pixel size of $150 \times 150 \mu\text{m}^2$, and an x-ray quantum efficiency of greater than 90% over the total energy range. The pixel detector is capable of full array readout in 10 μs , with a duty cycle (data acquisition to readout) of better than 99%.

Once they are developed, these detectors promise to increase the speed and accuracy of data collection at synchrotron sources relative to CCD systems. In particular, since the LBNL PAD is a digital

counting system, not an analog integrating system, the statistical precision of data collected on the PAD will be limited only by Poisson counting statistics, not by the imprecision and error of signal transfer steps within the instrument. The improved statistical precision of the PADs will have greatest impact on high-resolution data, such as those recorded in studies of charge densities in strongly diffracting crystals, but it will also enhance the quality of data recorded from weakly diffracting crystals. The PAD system also exhibits greater dynamic range than CCD systems. This will enhance the ability of a beamline to elicit high-quality MAD phasing and will improve the ability to acquire, simultaneously, the strong diffraction at low-resolution limits and the weak high-resolution terms.

2.5 Appendix: Flux-Density Limits in Protein Crystallography

Recent observations at the Advanced Photon Source (APS) at Argonne National Laboratory and European Synchrotron Radiation Facility (ESRF) in Grenoble indicate that frozen crystals can tolerate 3×10^{11} to 5×10^{11} photons/sec (12-keV x rays) onto an exposure field defined by a 200- μm square aperture (0.04 mm^2)—equivalent to a flux density of about 1×10^{13} photons/(sec·mm²). Substantially greater flux than this causes the onset of rapid, irreversible damage to the crystal sample and loss of diffracting power. Protein crystals vary, so this limit is not a rigid one, but at twice this flux density, all crystals suffer rapid deterioration in the beam. Below this value, crystals (frozen and maintained at 100 K) survive for hours. The explanation appears to be sample heating. Observations suggest that, at flux densities below about 1×10^{13} photons/(sec·mm²), thermally generated strain on the crystal lattice does not ruin the samples nor is their temperature rise sufficient to increase the mobility of radiation-induced free radicals—the presumed agent of most crystal damage. Rather, the crystals apparently reach an equilibrium state (in which temperature and thermal gradients permit heat deposition and extraction to be balanced) below any threshold of sample damage.

Bend-magnet sources at SSRL and the National Synchrotron Light Source (NSLS) do not deliver flux densities sufficient to damage protein crystals, but new insertion devices can exceed the damage threshold. In particular, the NSLS wigglers on Beamlines X21 and X25 the APS wigglers and undulators, the proposed SPEAR-3 wigglers at SSRL, and the ALS wiggler will destroy most protein-crystal samples unless the beams are attenuated or defocused.

To illustrate this point and to underscore the importance of a source intensity below the damage threshold, Figure 3 illustrates a hypothetical situation for a user acquiring MAD phasing data at various beamlines with crystals of various sizes. The assumptions made in this highly schematic illustration are that the user must spend one hour to prepare the experiment, that reading out each data frame requires 4 sec of dead time, and that the user is collecting four 250-frame data sets (one at each of four energies). We further estimate that an integrated x-ray dose of 1.0×10^{10} photon-mm on the sample is required to provide a “good” data frame (a lower dose will require less time, but at the cost of lower quality data; a higher dose will produce better data, but frames must be integrated for longer times). The shaded area illustrates the limits to flux density—in this region, the flux will damage the crystal sample. In the area below the damage threshold, as the flux increases, it takes progressively less exposure time to record a good data frame until, at about 10^{11} photons/sec, the total exposure time becomes a negligible fraction of the total time of the experiment.

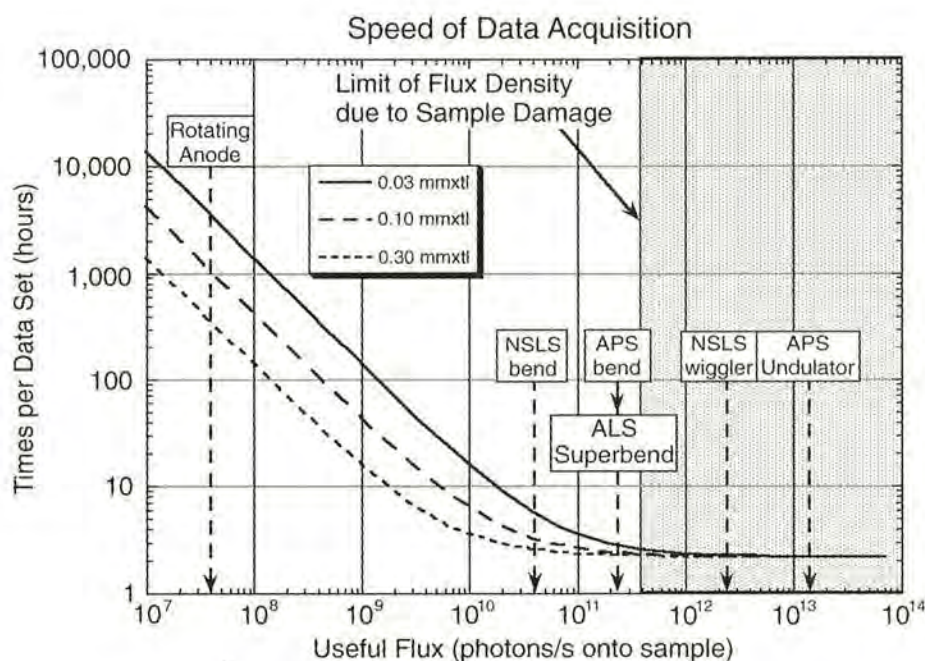


Figure 3. This highly schematic diagram illustrates that, under the assumptions made in the text, there is a limit to the useful flux density due to sample damage, so that there is no benefit to exceeding the flux-density limit. [Figure courtesy of Edwin Westbrook, Argonne National Laboratory.]

3. Soft X-Ray Microscopy: Advances and Opportunities in Cell Biology

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3.1 Introduction

In contrast to protein crystallography, which is a mature scientific field, x-ray microscopy is a rapidly evolving technique still in its infancy. New results suggest a promising role for soft x-ray microscopy. Short-wavelength x-ray imaging provides a spatial resolution more than five times better than that of visible light microscopy (See Table 1). Further, practical techniques have now been demonstrated that will open the door to investigations of keen interest to cell biologists. The Soft X-Ray Microscopy sub-group (1) discussed the exciting new technique for determining protein localizations in cells using soft x-ray microscopy, (2) identified specific biological questions to be addressed using x-ray microscopy, and (3) identified additional technological developments required for the continued advancement of x-ray microscopy in the biological sciences.

The sub-group concluded that the ALS, because of its brightness in the soft x-ray spectral region, is unique in the nation and therefore should be used to promote a program of national leadership and international competitiveness in soft x-ray microscopy.

Table 1. Comparison of features of biological microscopy techniques.

	Visible Light (Confocal) Microscopy	Electron Microscopy	Soft X-Ray Microscopy
Resolution	200 nm	0.1 nm to 0.3 nm (about 1 nm for noncrystalline biological material)	30 nm to 50 nm
Specimen Thickness	50 μm	Standard: 50 nm to 100 nm High Voltage: < 1 μm	10 μm
Hydration State	Hydrated	Dehydrated Hydrated (Cryogenic Only)	Hydrated
Physiology	Live	Dead	Dead

3.2 Challenging Questions in Cell Biology

X-ray microscopy is poised to make a major contribution to the understanding of cellular structure and function. The Soft X-Ray Microscopy sub-group discussed several central topics in cell biology that are ripe for investigation and identified particular ones that should be pursued further. The unique capabilities at the ALS make it essential to pursue these in Berkeley.

3.2.1 Structure/Function Analyses of the Cell Nucleus

Over the past two decades, nuclear architecture has been investigated using complementary microscopy techniques, including transmission electron microscopy (TEM) and, more recently, confocal microscopy. TEM techniques have enabled us to decipher the organization of nuclear domains and higher levels of chromatin arrangement, and confocal microscopy has permitted us to study the dynamics of nuclear components in the entire nucleus. In addition, immunolabeling and *in-situ* hybridization techniques applied using both types of microscopy have underscored the importance of

nuclear organization for nuclear function. The possibility that higher levels of chromatin arrangement and the compartmentalization of nuclear function are related to an underlying structure has been raised. Twenty-four years ago, TEM studies demonstrated that an insoluble, organized structure referred to as the nuclear matrix (NM) was left behind after the removal of soluble proteins, as well as most of the chromatin. Numerous components of this NM fraction, either permanent or transitory, have now been identified. However, the existence of an organized NM that could play a role in nuclear and, ultimately, cellular function is still controversial. This controversy is based on the fact that it is necessary to apply harsh preparation procedures to samples in order to visualize the NM in the electron microscope. The ability to simultaneously image chromatin components and NM components using soft x-ray microscopy in hydrated, non-extracted, and non-sectioned cells (see Figure 4) will bring an essential insight to the study of the interrelationship between nuclear organization and cellular function.

3.2.2 Cell-Extracellular Matrix Interactions and Signaling

Over the last 15 years, studies by LBNL researchers have shown that a reciprocal dialog exists between the mass of fibrous and globular proteins outside the cell (the extracellular matrix or ECM) and the inside of the cell. Recent data indicate that the disruption of this dialog can lead to tumor formation. Restoration of the cell's delicate microenvironment in turn can revert tumors to cell clusters resembling the normal phenotype. Thus a novel strategy to control unchecked cell growth and function has been elucidated. The implications of these discoveries are enormous, both as a tool for the further elucidation of normal cell growth and differentiation and as an assay to screen libraries of compounds of potential therapeutic value against cancer. This is one dramatic example where soft x-ray microscopy can shed additional light on basic molecular mechanisms since the x-ray microscope has the capability to view the cell-cell and cell-ECM interactions at higher resolution than light microscopy.

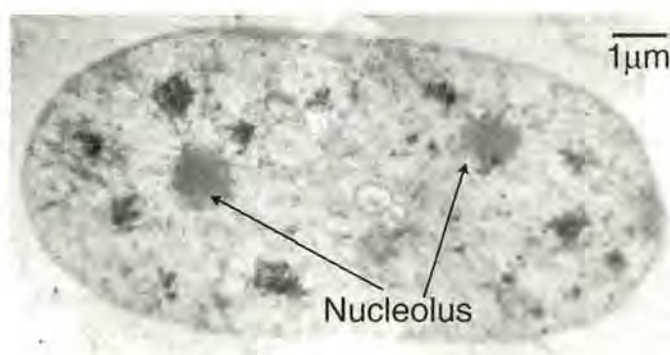


Figure 4. Nucleus of human mammary epithelial cell (S1-50) labeled for splicing factor. This image was obtained from a whole, hydrated cell. Structural details of the nucleus, including nucleoli can clearly be identified in addition to the label, which appears dark. [Figure courtesy of C. Larabell, D. Hamamoto, S. Lelièvre, and W. Meyer-Ilse, LBNL.]

3.2.3 Host-Parasite Interactions

The ability of soft x-ray microscopy to examine thick cells provides a unique opportunity to examine host-parasite interactions. This has been demonstrated at the ALS by the studies of Cathie Magowan, Werner Meyer-Illse, and colleagues at the LBNL Center for X-ray Optics, who examined the way in which the malaria parasite (*Plasmodium falciparum*) develops in human red blood cells. The ability to examine parasites within the host, without risking the artifacts that accompany embedding and sectioning protocols, provides a powerful tool for understanding these important cell-cell interactions. Unique views of the infected blood cells revealed new information about the contribution of the membranes of red blood cells to parasite development that were not previously detected using other forms of microscopy.

3.2.4 *In-Situ* Hybridization Using X-ray Microscopy

Fluorescent *in-situ* hybridization (FISH) is a widely used method to assay gene expression using light microscopy. The method has been applied in a variety of situations where the tissue distribution of gene transcripts needs to be determined with a reasonable degree of spatial resolution. It has also been used to compare the distribution of gene transcripts in normal and tumor cells. The ability to obtain such information using the increased spatial resolution of x-ray microscopy is of the utmost importance. Development of an *in-situ* hybridization technique for x-ray microscopy (XISH) that is based on silver-enhanced, gold probes is in progress at LBNL by Carolyn Larabell and colleagues and will be a significant breakthrough for the fields of cell and molecular biology.

3.2.5 The Origin of DNA Replication

Visualization of the origin of DNA replication with its associated complex proteins is of great interest for the understanding of basic cell functions. The pathways of these complexes during the replication process have never been seen. The structures of interest are larger than nucleosomes, which are about 11 nm in size, and will be in the reach of soft x-ray microscopy. They would be made up of many proteins and DNA, and new ideas might be needed for "staining" the complexes to take advantage of the x-ray imaging. Antibody-labeled gold markers could be used as a starting point, since antibodies of most of the components of the replication process are available.

3.2.6 Sperm

X-ray microscopy still has a great deal to offer to an analysis of normal sperm development and to characterizing the biochemistry (and different classifications) of male infertility. Chemical imaging by means of near-edge x-ray absorption fine-structure spectroscopy (NEXAFS, also known as XANES) should help identify the fate of some transient parts of proteins that disappear during the course of sperm-cell maturation (leader sequence of protamine 2). The procedure would be to (1) check for the normal progression of this process in infertile samples or identify (and investigate) types of infertility that result from improper ratios of protamine 1 and 2 or improper displacement of histones by protamines and (2) identify cells produced by infertile males that do not contain properly disulfide-bonded protamines. With the ability to measure the mass of the nucleus, once we are able to do three-dimensional imaging, we could use x-ray microscopy to determine the density of packing of chromatin inside the nucleus as an indicator of improper chromatin condensation.

3.3 Environmental Biology

The ability to study hydrated systems with high spatial resolution, combined with the ability to map certain elemental and chemical properties of the sample, makes soft x-ray techniques very valuable for environmental biology. Many species of bacteria can oxidize or reduce transition-metal ions, especially iron and manganese. Imaging with photon energies either above the absorption edges of the transition metal or in the water window for carbon-rich microorganisms provides specific contrast of the metal-containing particles or the organic material. Only soft x rays provide the ability to image these processes with the necessary resolution in the hydrated state.

3.4 Experimental Opportunities with X Rays

Use of shorter wavelength radiation, such as electrons or x rays, provides significantly better spatial resolution than visible-light microscopy. Exploring the utility of chemical or elemental imaging by combining spectroscopy with high spatial resolution will give x-ray microscopy an enormous edge in usefulness. Chemical or elemental imaging cannot be done at the level of whole cells by electron microscopy or other conventional techniques, yet several of the questions discussed above will have chemical/compositional changes associated with it.

The penetration depth of x rays in matter varies significantly throughout the x-ray photon-energy range. We will therefore discuss soft x rays (below about 2.5 keV) and hard x rays (above about 2.5 keV) separately. The transition region between soft and hard x rays is indistinct, and lately also called intermediate x rays.

3.4.1 Soft X-Ray Microscopes Provide High Spatial Resolution

Among all types of electromagnetic radiation, only soft x rays provide a spatial resolution exceeding that of visible-light microscopes for thick samples. Most biological work uses x rays in the water window, that is the range of photon energies between the K-shell absorption edges of carbon (284 eV) and oxygen (543 eV), where organic matter absorbs nearly an order of magnitude more than water. For x-ray energies just below the oxygen edge (e.g., 517 eV, 2.4-nm wavelength), the penetration depth of x rays is also ideally suited to image whole cells with a thickness of a few microns. Contrast in the water window can be either from absorption or phase shift. Microtomography with soft x-ray transmission microscopes has also been demonstrated and provides three-dimensional information with unprecedented spatial resolution.

3.4.2 Elemental and Chemical Mapping

High-resolution absorption spectra from any point on the specimen can be obtained by positioning the specimen to the appropriate spot and scanning the monochromator of a scanning transmission x-ray microscope (STXM). Spectra near the carbon, nitrogen, and oxygen absorption edges are rich in structure (NEXAFS), that provides sensitive information regarding local chemistry. By collecting images at several energies in this region, it is possible to map particular components within the specimen. Xiaodong Zhang of the State University of New York, Stony Brook, et al. examined the distribution of protein and DNA, thereby demonstrating this capability in mammalian sperm nuclei. Figure 5 shows the spectra of different amino acids at the carbon K edge, as obtained with the STXM at the NSLS.

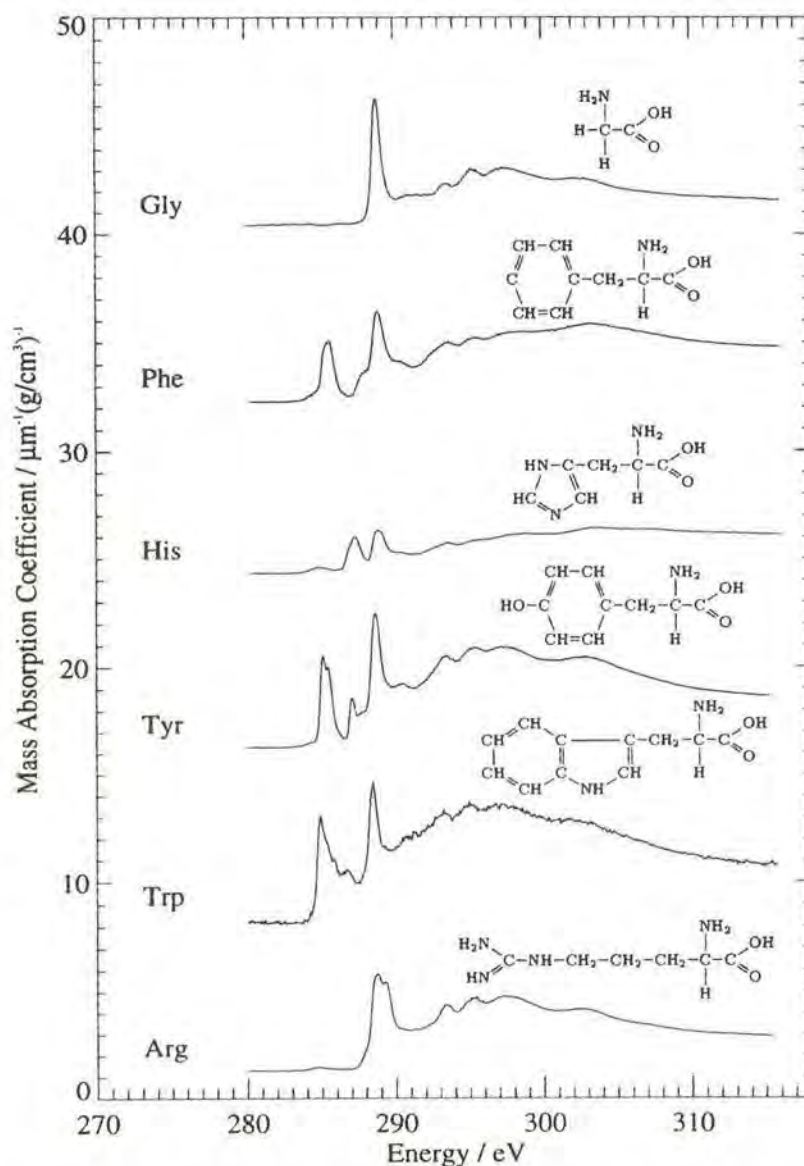


Figure 5. Carbon-edge x-ray absorption near-edge spectra and chemical structure of the six amino acids: glycine (Gly), phenylalanine (Phe), histidine (His), tyrosine (Tyr), tryptophane (Trp) and arginine (Arg). The spectra have been displaced vertically by multiples of eight units. [Figure courtesy of J. Boese, State University of New York, Stony Brook; data from Beamline X-1A at the NSLS.]

3.4.3 Hard and Intermediate X Rays: Spectroscopy, Fluorescence, and Phase Contrast

X-ray fluorescence microscopy and spectromicroscopy with harder x rays have many unique and attractive qualities. In particular, these techniques can provide information on the spatial distribution, oxidation state, chemical environment, and chemical transformations of trace elements.

Although harder x rays do not provide sufficient absorption contrast for high-resolution transmission x-ray microscopy and phase contrast is also reduced when used with harder x rays (but to a lesser degree), the presence of K-shell absorption edges makes harder x rays very useful for spectroscopic methods with spatial resolutions down to about 1 μm . Intermediate-energy NEXAFS at the K-edge

of transition metals provides information about the oxidation state, for example, which is related to solubility and toxicity in plants and microorganisms.

The sensitivity advantage of x rays with respect to electron and proton probes is three to four orders of magnitude for elements with atomic numbers $10 < Z < 40$ and greater than four orders of magnitude for heavier elements. K-edge x-ray spectroscopy is not a new method but its capability is being rapidly extended at the present time because of improvements in available the x-ray source brightness and in the performance of optical schemes for focusing the x-ray probe. With the ALS as the source and the best mirrors and zone plates to form the probe, one can expect parts-per-million sensitivity for the lower Z elements of biological interest (especially sodium, phosphorus, sulfur, chlorine, potassium, and calcium) and parts-per-billion sensitivity for higher Z elements. Mirrors provide the best wavelength tunability and flux (i. e., best sensitivity) at resolutions of 1 μm currently, while zone plates offer resolution from 0.25 μm to about 0.1 μm in the best case to date.

All the methods discussed above use contrast methods that are intrinsic to the sample. As discussed above, specific labeling and gene mapping are also possible with x-ray microscopes.

3.4.4 What Are the Experimental Alternatives to Soft X Rays?

Soft x-ray microscopy is complementary to other methods. The spatial resolution is between that of electron and (confocal) visible-light microscopes (see Table 1). Many efforts are aiming to improve the resolution of visible-light microscopes. Most notable are near-field scanning optical microscopes (NSOM) and two-photon confocal microscopes. NSOM provides very good spatial resolution, but only from a thin layer at the surface of the sample. Although an improvement over conventional confocal microscopes, two-photon microscopes do not reach the resolution provided with present soft x-ray microscopes.

Electron microscopy clearly has a spatial resolution superior to x-ray microscopes. The limited penetration depth of electrons (including that in high-voltage microscopes) as compared to x rays, however, prevents high-resolution imaging of whole cells. Serial sectioning is used to overcome this limitation. However, x-ray microscopy of individual whole cells (about 10 μm thick) does not require sectioning.

3.4.5 Further Utilization of High-Resolution Labeling Techniques Is of Utmost Importance

The use of fluorescently labeled antibodies to localize proteins in the light microscope has led to major advances in the understanding of cell structure and function. The amount of information that can be gained from these analyses, however, has been limited by the spatial resolution of the light microscope. To obtain higher-resolution information about the localization of proteins, silver-enhanced, gold-conjugated antibody probes can be used in an x-ray microscope. Henry Chapman and Chris Jacobsen pioneered this technique at Brookhaven National Laboratory using dehydrated cells. Larabell and Meyer-Ilse extended the use of silver-enhanced, gold probes to localize proteins in hydrated cells using the soft x-ray microscope XM-1 at the ALS. This technique, which is a modification of a labeling protocol previously used to localize proteins in the transmission electron microscope, proved to be a powerful approach for examining protein localizations in the x-ray microscope. At the workshop, the Brookhaven group reported using such probes to label microtubules in dehydrated cells that were then examined in the scanning x-ray microscope at the NSLS, and the Berkeley group presented its results based on similar probes to label microtubules in hydrated, whole cells for examination in XM-1. These data demonstrate the proof-of-principle *that x-ray microscopy can be*

used to obtain high-resolution information about the distribution of proteins in whole cells. The Berkeley group extended its studies to obtain high-resolution information about the distribution of proteins in the nuclei of cells. This is an extremely exciting development since nuclear organization, although of the utmost importance, is very poorly understood, owing in large part to the fact that it has been difficult to analyze nuclear structure with standard microscopic techniques. The Berkeley group illustrated the power of the x-ray microscope to visualize the structural composition of whole, hydrated nuclei—a feat not possible with other known types of microscopy. In addition, the group demonstrated the capacity to label proteins in whole, hydrated nuclei using the Ag-enhanced, gold labeling technique. This is a major breakthrough since many of the structure/function studies of the nucleus done to date have been criticized because of the artifacts associated with the elaborate preparation techniques required to visualize the nucleus in the electron microscope. The ability of the soft x-ray microscope to visualize labeled cytoplasmic and nuclear proteins with respect to the underlying cell structures has demonstrated that soft x-ray microscopy can bridge the gap between light and electron microscopic analyses and can obtain information about protein localizations at higher resolution than possible with light microscopy but without the extensive cell preparations required for electron microscopy.

3.5 Instrumental Challenges

X-ray microscopy is a new tool to study cells in a new way and to discover new, even unexpected information because of the high-resolution images it can provide from biological materials. Its usefulness lies in the fact that it compliments other more well-established techniques and at the same time pushes the frontiers of knowledge. State-of-the-art microscopes and support laboratories are needed, to use the x-ray methods. The high resolution of the microscopes is as important as convenient access and the quality of the light source. The utility of the facility is measured by the strength of the weakest link. The instrumental technology has reached a level that already makes routine studies possible, and further investments in instruments will leverage the utility of third-generation light sources like the ALS. Directions for further developments are discussed below.

3.5.1 Improve Zone-Plate Lenses for Soft X Rays

Present zone-plate lenses provide a resolution in the 30-nm to 50-nm range. Future developments of zone-plate lenses are aiming to reach 10-nm to 20-nm resolution. The resolution of “conventional” microscopes, such as XM-1 at the ALS and the University of Göttingen’s x-ray microscope at the Berlin Synchrotron Radiation Facility, (BESSY) is limited by the zone-plate optics only. These instruments will therefore immediately benefit from improvements in zone-plate lenses. Scanning x-ray microscopes will need improved scanning stages in addition.

3.5.2 Cryogenic Sample Preservation

Cryogenic sample preservation is crucial for the application of x-ray microscopy in the biological sciences, since it reduces sample damage at high resolution and when making multiple images. Cryogenic sample stages are therefore either operational or under construction at BESSY, NSLS, and the ALS. Multiple images of hydrated material, as needed for tomography, will definitely require cryogenic preservation. Figure 3 shows the image of an algae imaged at low temperatures with the Göttingen x-ray microscope at BESSY.

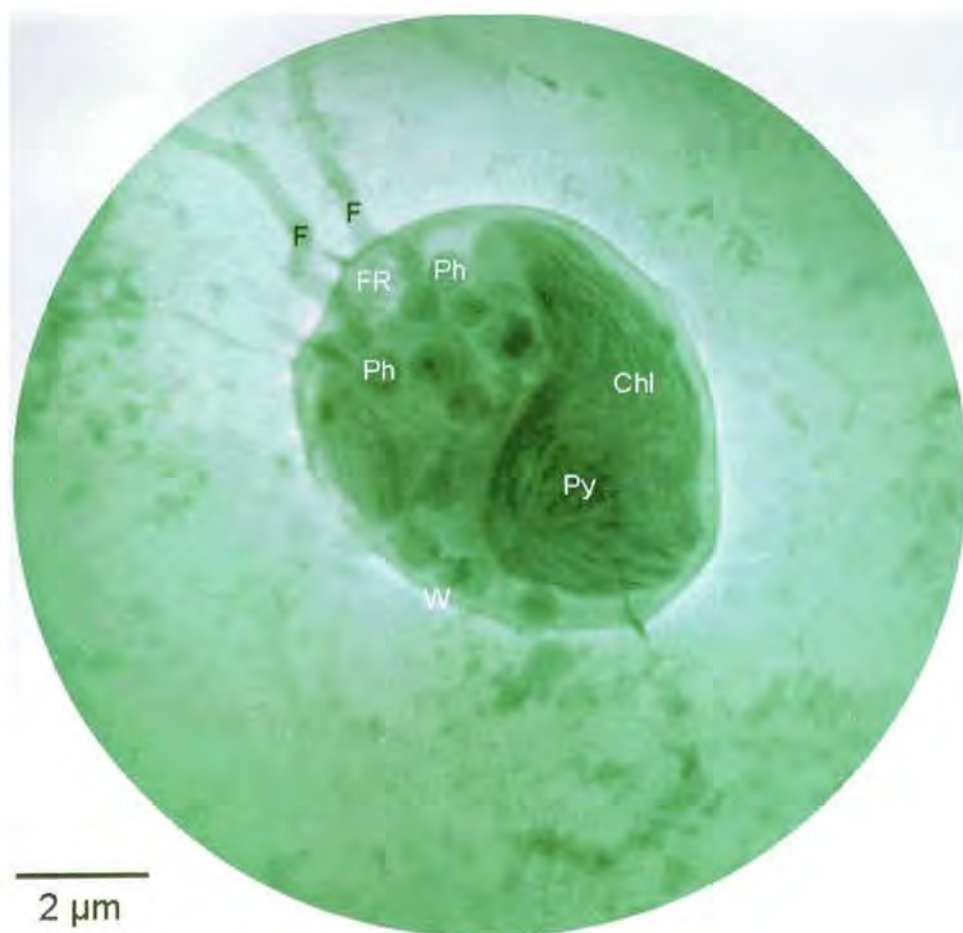


Figure 6. Algae fixed and imaged at low temperatures with the Göttingen x-ray microscope at BESSY in Berlin, Germany. *F* = Flagellum $\varnothing=300$ nm, *FR* = Flagellar root, *Chl* = Chloroplast, *Py* = Pyrenoid, *Ph* = Dense phospholipid vesicles, *W* = Cell Wall. [Figure courtesy of G. Schmahl, University of Göttingen.]

3.5.3 Tomography

Soft x-ray microscopy provides possibilities to obtain three-dimensional information within whole cells. High-resolution tomography has recently been demonstrated using the Göttingen x-ray microscope at BESSY. An early demonstration of tomography with cryogenic samples was made at Beamline X-1A at the NSLS.

3.5.4 Undulator-Based Microscopes

Scanning soft x-ray microscopy offers capabilities complementary to conventional microscopes, such as XM-1 at the ALS and the Göttingen microscope at BESSY. In a scanning x-ray microscope, a microbeam is formed, and the specimen is raster scanned across it. Originally developed by the Stony Brook group at the NSLS, such a system is now also in operation on Beamline 7.0.1 at the ALS. Scanning is also compatible with other schemes, such as dark-field and luminescence micros-

copy. An optimized scanning microscope at the ALS would take about 5 seconds to record a picture with 1000×1000 pixels, with 1000 photons detected per pixel. Such performance with high resolution is highly desired for biological applications, but it requires developmental work for the scanner, beamline, and detector systems.

3.5.5 Precision Instrumentation and Support Laboratories

Soft x-ray microscopy facilities need to be easily accessible for users who might not be familiar with synchrotron-radiation facilities. Precision instrumentation with an easy user interface, software, and data-handling capabilities are crucial, as are support laboratories that are set up for sample handling and preparation.

3.5.6 Hard X-Ray Instrumentation and Other Techniques

Soft x-ray imaging provides high spatial resolution with the best overall utility. Imaging methods that use small pinholes might reach a 10-nm resolution before zone-plate optics with the same resolution are available. The low efficiency of such methods, however, will limit these methods to a very small number of special investigations. Intermediate and harder x rays can also be used if x-ray fluorescence or K-shell spectroscopy are used. Hard x-ray phase zone plates with a spatial resolution of about 0.1 μm and focusing efficiency better than 33% are the present state of the art. Whereas the ALS is the premier source for soft x rays, the activities in the intermediate and hard x-ray ranges should be coordinated with the other synchrotron facilities.

3.6 The Role of the ALS and Berkeley Lab

3.6.1 Undulator-Based Facility

ALS undulators are the brightest sources for soft x rays in the nation. Scanning microscopes depend on brightness because they require spatially coherent radiation. The ALS is therefore the ideal source for these most demanding soft x-ray microscopes. Several proposals to build an undulator-based soft x-ray microscopy facility have been discussed over the past years, the latest one being headed by the environmental-science community (see the report of the Working Group on the Environmental and Earth Sciences). The biological community would benefit from such an instrument and supports an interdisciplinary collaboration to build such a facility.

Since the advantages of high-resolution microscopy not only benefit the biological community but also environmental, materials, chemical, and engineering sciences, special attention has to be put into long-range planning. As demonstrated with existing microscopes, these different applications are both compatible and best served with an instrument that matches the performance of the ALS.

3.6.2 Current Capabilities

A bend-magnet-based x-ray microscope (XM-1) is operational and in use with several biological-research programs. This instrument has begun to attract a growing biological user community. Although the optical layout of XM-1 is identical to the Göttingen microscope at BESSY, its precision instrumentation makes it to the most versatile, easily accessible instrument in the world. It is expected to complement future scanning microscopy activities at the ALS. A cryogenic sample stage for XM-1 is under development and has produced first results. Adding tomography capabilities should also further develop this instrument.

The ALS not only offers unique brightness but also necessary support laboratories, and it is also close to local research groups in both biology and technology, thus providing a fruitful environment for successful collaborations.

3.6.3 Relationship to Other Synchrotron Radiation Facilities

X-ray microscopy depends on the quality of the light source. New generations of synchrotron radiation facilities therefore drive new microscope developments. The group at the University of Göttingen, which pioneered soft x-ray microscopy with synchrotron facilities and operates a microscope at BESSY, is planning an x-ray microscopy facility at BESSY II, which is a third-generation machine very similar to the ALS. The microscope at BESSY II will use a beamline with a 4.1-cm-period undulator. An improved conventional microscope with improved spatial resolution, short exposure times, and improved spectral resolution is fully funded and under construction. A scanning microscope is in the planning stages.

Soft x-ray scanning x-ray microscopy was pioneered by the State University of New York at Stony Brook at the NSLS, a second-generation machine. Harder x-ray facilities are located at the APS and the European Synchrotron Radiation Facility (ESRF).

3.7 Recommendations

3.7.1 Fully Support Present Activities in Biological Soft X-Ray Microscopy at the ALS

Biological microscopy research at the ALS presently uses the bend-magnet based microscope XM-1. This instrument should continue to be used for biological research. We emphasize that the newly developed techniques for labeling, cryogenic sample preparations, and future plans for three-dimensional imaging are expected to play an important role in biology.

3.7.2 Construct an Undulator-Based Microscopy Facility

The biological user community supports an undulator-based x-ray microscope facility. A collaboration with other fields, (environmental, materials, chemical sciences) will be beneficial for biology. Both scanning and conventional microscopes would be possible and serve complementary needs. The scanning microscope should be built first to serve the complementary needs with the existing microscope XM-1.

3.7.3 Collaboration with Other Light Sources

The ALS clearly is the premier facility for soft x-ray microscopy and therefore ideally suited for the biological research described here. Other facilities either offer opportunities in the hard x-ray range or have already developed specialized instruments that should be used in collaboration. The unique resources for soft x rays at the ALS need to be utilized with care. Experiments that do not require the ALS might be better done at other facilities.

4. Biological and Chemical X-Ray Spectroscopy

Facilitator: Stephen Cramer, University of California, Davis

Working-group members: Uwe Bergmann, Lawrence Berkeley National Laboratory; Heinz Frei, Lawrence Berkeley National Laboratory; Melissa Grush, University of Tennessee; Keith Hodgson, Stanford University; Brian Kincaid, Lawrence Berkeley National Laboratory; Melvin Klein, Lawrence Berkeley National Laboratory; James Penner-Hahn, University of Michigan; Charles Tarrio, National Institute of Standards and Technology; Vittal Yachandra, Lawrence Berkeley National Laboratory.

4.1 Introduction

The bioinorganic-chemistry community was among the first to adopt synchrotron-based extended x-ray absorption fine-structure spectroscopy (EXAFS) as a routine structural tool. The X-Ray Spectroscopy sub-group discussed the important current issues for biological and inorganic chemistry and tried to define the important science in these areas that can be addressed by x-ray spectroscopy.

Some of the questions discussed by our group included:

- What are the important research areas (now and in the future) in biological and inorganic chemistry that can be addressed by x-ray spectroscopy?
- In what areas should national resources for x-ray spectroscopy be developed?
- What x-ray spectroscopy capabilities are best developed at the ALS?
- What is the expected impact on chemistry and for society?

4.2 Important Research Areas

Metals are important in biology both for their beneficial role in enzyme active sites and structure and for the negative effects of enzyme inhibition or disruption by heavy metals or normally benign metals at unhealthy concentrations. Metalloenzymes play important environmental roles as pivotal agents in the nitrogen, sulfur and carbon cycles, and in the production and consumption of greenhouse gases, such as methane. It is also worth noting that enzymes are a billion-dollar business in the United States alone. Thus, in the three critical areas of (1) human health, (2) environmental impact, and (3) commercial potential, a better understanding of enzymes and related model chemistry could have profound impact. X-ray spectroscopy is an important tool for expanding our knowledge because it can answer the following important questions:

4.2.1 What Are the Molecular, Electronic, and Magnetic Structures of Enzyme Active Sites?

A good example of this kind of problem is the oxygen-evolving complex of photosystem II. Based on their EXAFS work and other information, Melvin Klein at LBNL and co-workers have proposed a model for the structure of this complex (see Figure 7). K-edge EXAFS is valuable for defining the metal-neighbor distances. Investigating the fine structure in the chlorine and manganese K-edge region (NEXAFS) can yield important information about the electronic structure of this complex. Many new experiments such as EXAFS at the manganese L edge and x-ray magnetic circular dichroism (XMCD) spectroscopy of manganese, have been planned for the elliptical-undulator beamline at the ALS.

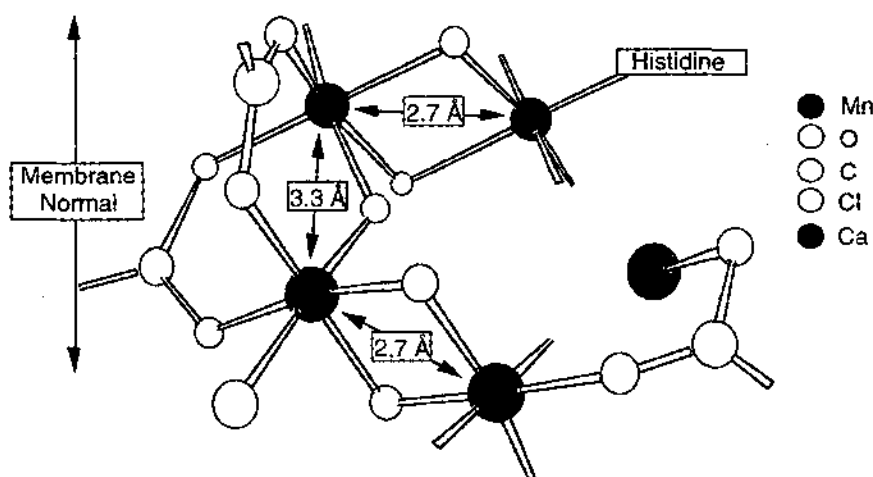


Figure 7. Proposed model for the manganese/calcium/chlorine cluster in the evolution of photosynthetic oxygen. [Figure adapted from Yachandra, DeRose, Latimer, Mukerji, Sauer, and Klein, *Science* **260** (1993) 675.]

4.2.2 How Do the Concentration and Chemical Speciation of Elements Change Across an Organism?

Living systems are not homogeneous, and the gradients of metals and other elements across an organism reveal important information about structure and function. A great deal has already been done by fluorescence microscopy—for example, many beautiful studies of calcium waves in different organisms. However, x-ray spectromicroscopy can discover information inaccessible by other means. For example, James Penner-Hahn of the University of Michigan has used x-ray absorption to study the distribution of zinc in sperm cells. He has seen clear gradients across the cells. Furthermore, the zinc NEXAFS changes at different locations, indicating a spatial variation in the different chemical forms of zinc.

4.2.3 How Does the Chemical Speciation of Elements Change Over Time?

The time dependence of chemical species in an organism is just as important as the spatial variation. X-ray spectroscopy can provide valuable information about species that difficult to observe by other spectroscopies. For example, Klein and coworkers have used sulfur K-edge spectroscopy to monitor changes in the mix of reduced and oxidized sulfur species in the blood before and after drug administration. There are many situations in microbiology where one would like to follow the change in metal speciation after induction of specific enzymes—for example, the change in molybdenum chemistry after induction of the genes for nitrogen fixation.

4.3 Needed National Resources for X-Ray Spectroscopy

4.3.1 Detectors

On one point the sub-group was unanimous—spectroscopy at the moment is just as limited by detectors as it is by beamlines. New detectors need to be developed that are faster and that have higher energy resolution. Since they will be shared by many users, the detectors also need to be “robust” and “supportable.”

4.3.2 High Energy Resolution

There are surprisingly few high-resolution and high-flux beam lines in the country. The best examples are probably Beamlines X-25 and X-27 at NSLS. Many of the beamlines at SSRL are high-flux, but their

resolution is degraded by the pre-crystal focusing optics. For spectroscopic applications, such as NEXAFS, resonance fluorescence, and x-ray Raman spectroscopy, better energy resolution is important.

4.3.3 The 2-keV to 3-keV Region

Another important area that is poorly served at the moment is the 2-keV to 3-keV region, which contains important edges such as the sulfur and chlorine K edges and molybdenum L edges. An ALS beamline should be designed to maximize flux in this region.

4.3.4 A Spectromicroscopy Capability

Although the ALS is pushing the state of the art in soft x-ray microscopy, there are many important hard x-ray experiments where micron-scale resolution would be useful. A beamline capable of moderate resolution spectromicroscopy should be developed.

4.3.5 A Time-Resolved Capability

The ALS should help develop a time-resolved x-ray absorption capability on the millisecond-to-seconds scale. Many biological processes occur on this time scale, and making rapid x-ray absorption routinely available to users would lower the barriers to this kind of work.

4.3.6 Newer Spectroscopies

High resolution x-ray fluorescence and inelastic scattering look promising for site-selective x-ray absorption and better understanding of electronic structure. Secondary monochromators should be available to general users on a beamline to make these experiments possible.

4.3.7 User Issues

There are also many user-related issues that would make the ALS a more productive place for x-ray spectroscopy. Our group noted that other facilities such as ESRF, NSLS, and SSRL provide some of the following:

- Detectors and chambers for spectroscopy users.
- Support staff for spectroscopy science.
- Support for spectroscopy software.
- Support for spectroscopy detector development.
- ESRF and NSLS have mail-order XAFS; SSRL has rapid-turnaround service.

The ALS should consider whether it can do in the soft x-ray region what these facilities do for hard x-ray users.

4.4 Summary of Conclusions

The elliptical undulator beamline should be completed as quickly as possible.

There is a strong need for a high resolution hard x-ray beam line at the ALS to cover the 2 keV to 10 keV region.

Better detectors are needed to take full advantage of both of these beamlines.

Although they are not at the frontiers of technology, x-ray spectromicroscopy on the 1- μ m scale and kinetics on the millisecond scale would make very practical contributions to biological spectroscopy.

Working Group on Atomic, Molecular, and Optical Physics

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1. Introduction

Third-generation synchrotron light sources have opened up research frontiers that may hold the answers to fundamental questions about structure and dynamics in atomic, molecular, and optical (AMO) physics. The advanced spectroscopies being developed at the Advanced Light Source (ALS) give us the ability to control and probe atomic and molecular processes with unprecedented precision. In particular, the spectral resolution, brightness, broad tunability, and polarization control generate novel avenues for the study of tailored states, inner-shell processes, and nonperturbative electron interactions. Driven by the high brightness of the ALS, a whole new world of vacuum-ultraviolet (VUV) and soft x-ray physics is emerging through the development of combined techniques to excite, select, and probe atoms, molecules, and clusters.

Synchrotron-based AMO physics has a long history of producing new advances in our understanding of fundamental physical phenomena. For example, Madden and Codling, in their 1963 experiments using VUV synchrotron radiation, discovered two new series of autoionizing resonances in doubly excited helium. The characterization of these resonances led theoreticians to develop a new classification scheme for doubly excited states that resulted in a new understanding of correlated electron motion. Some of the first experiments at the ALS produced much higher resolution spectra of these same series; these new spectra appear to show signs of the elusive phenomenon of quantum chaos. This work is an example of the surprises and new physics that will be uncovered by using the unique capabilities at the ALS. These new capabilities have already resulted in significant advances and tests of fundamental assumptions in double photoionization and few-body dynamics, in inner-shell photoionization dynamics and sub-natural-linewidth spectroscopy, in doubly and triply excited states, and in the site-specific excitation and characterization of chemical activity in molecules.

In short, AMO physics at the ALS is already a vibrant activity. In less than three years, AMO research at the ALS has resulted in more than 60 refereed articles, including 12 Physical Review Letters that illustrate the breadth and depth of this field. The initial productivity has been remarkable, since it was demonstrated during a period when the relevant beamlines were first being commissioned and sophisticated end stations were still under construction. This fast start reflects the excitement and enthusiasm felt by AMO researchers who now see a wealth of new capabilities engendered by the ALS itself and by state-of-the-art beamlines and detectors.

2. Outstanding Scientific Issues

The scientific motivations in AMO physics fall into two major categories. The first involves the fundamental quest to understand basic phenomena in atomic and molecular systems in their own right. Many of these phenomena remain beyond the realm that can be successfully tackled by present-day theoretical techniques. The second category of motivations concerns atomic, molecular, and optical phenomena that impinge on other areas. Questions in sister fields of science often hinge on a determination of how an atom or molecule will behave in a specific context, often one in which the system is excited to an energy range well above that of typical electronic or chemical binding energies. In this second category, the main goal of the research is to obtain relevant reaction rates or cross sections directly, or to provide critical benchmarks to improve theoretical techniques to the point where cross sections can be calculated to the accuracy desired. In the following we discuss a number of scientific problems on the horizon in AMO science that are driven by at least one of these underlying motivations.

The substantial improvements in sophisticated new spectroscopies, which have only now become possible with the high brightness of the ALS, are already providing new challenges to existing theoretical methods. In some systems, for instance, existing theoretical predictions of three-particle breakup cross sections differ by a factor of two or more. The new high-resolution, multicoincidence experiments that can be performed at the ALS allow the essential components of complex processes to be isolated, which both simplifies and clarifies the comparison with theory. Propensities for final-state energy and momentum sharing can now be explored and unraveled for complex systems. The multidimensionality of the experimental observations also suggests the need to develop new visualization methods for the display and comprehension of complex data sets. New experimental results from the ALS not only provide an important touchstone for such developments but literally drive them. In the following discussions, we present a set of scientific problems whose solutions require the use of state-of-the-art techniques in conjunction with the characteristics of the ALS.

2.1. Photon-Ion Interactions

2.1.1 Positive Ions

More than 99.9% of the matter in the solar system exists in an ionized plasma state. Knowledge of the structure and interactions of ions therefore has both fundamental and practical importance. Because ionization by photons plays a key role in many astrophysical and laboratory plasma environments, accurate VUV and x-ray opacities are critically needed as input data for the plasma modeling. Quantitative studies of ionic photoexcitation and photoionization also serve to test and advance theoretical descriptions of atomic structure, including multichannel resonance phenomena and post-collision interactions. Studies of ions can be conveniently systematized along isoelectronic or isonuclear sequences. Such systematic studies can be used to highlight specific aspects of ionic structure and interaction. For example, as one moves from lighter systems where electron interactions dominate to heavier systems where relativistic effects are more important, the evolution of certain effects as a function of the ionic charge reveals regularities that are often difficult to spot in the spectrum of a single atom or ion. The most definitive tests of quantum electrodynamics (QED) involve transition energies in multiply ionized atomic systems. In addition, photoionization of transition-metal ions is expected to display large qualitative differences from the alkaline-earth atoms, based on hints from measurements with second-generation sources. Measurements of the ratio of multiple- and single-ionization cross sections critically test our understanding of joint electron-electron motions, which are crucial for the very existence of negative ions.

Another type of experiment for molecular ions could measure the correlated center-of-mass motion and energy sharing of the three massive particles H^+ , H^- , H^+ formed in the dissociation of a beam of excited H_3^+ using triple-coincidence techniques. These types of correlation studies can be extended to other massive three-body molecular systems, of course, and are not limited to final states where all particles are charged.

2.1.2 Negative Ions

Photoexcitation and photodetachment processes in negative ions stand out as an extremely sensitive probe and theoretical testbed for the important effects of electron-electron interactions because of the weak coupling between the photons and the target electrons. Numerous studies of outer-shell photodetachment have been conducted using lasers, but no experiment has ever been conducted on inner shells of negative ions using synchrotron radiation because of the very low count rate associated with these experiments. Negative ions present a severe theoretical challenge since the independent-electron model is inadequate for even a qualitative description of their properties. In some instances, the electron-correlation energy contribution to the electron affinity is as large or even larger than the electron affinity itself. With the high flux and brightness of the ALS, detachment resonances associated with excited-state channels well above the first threshold can now be measured for key few-body systems like H^- , He^- , and Li^- .

A permanent multi-user end station is currently being developed by the HRAMO (high-resolution atomic, molecular, and optical) group at the ALS to study photon-ion interactions at ALS Beamline 10.0.1, which is illuminated by a U10 undulator. This facility opens up new and exciting possibilities for studying either negative or positive ions, including multiply charged ions and a variety of triatomic systems. Three-body half collisions can be studied for a variety of prototypical systems as a function of the energy above a dissociation-limit threshold, even (signal permitting) as a function of the orientation of the initial molecular system relative to the polarization state of the initial photon.

This end station, when coupled with the high flux of the ALS, will be the first facility in the world that provides exciting opportunities for pioneering experiments with negative ions (including clusters).

2.2 Inner-Shell Spectroscopy of Atoms and Molecules

Recent improvements in synchrotron-radiation capabilities have generated exciting advances in atomic and molecular core-hole spectroscopy. Excitation selectivity in energy, in momentum, and in spin-polarization has opened the door to a wealth of new information. The following examples highlight some of the diverse possibilities of this broad scientific area.

2.2.1 Spin-Polarized Auger Spectroscopy

During the past two decades, spin polarization of valence photoelectrons excited by circularly polarized light has been studied actively. Owing to the absence of any intense source for circularly polarized VUV or x-ray radiation, the only inner-shell spin-polarized experiments conducted during the past three years were for xenon using the European Synchrotron Radiation Facility (ESRF), the third-generation source in Grenoble, France. When highly differential detection methods are coupled with circularly polarized light from the ALS, the spin-polarization of atomic or molecular Auger electrons in atoms and molecules makes it possible to track down the radiationless decay mechanisms of an inner-shell excitation. In some cases, this spectroscopic method can track the apportionment of both angular momentum and energy among photofragments. Such experiments test the importance of relativistic effects in the atomic or molecular structure, as well as in the photoejection process itself. They also permit a test of models of the angular-momentum coupling for states with two holes. When this experimental tool is applied to transition-metal elements, it can provide an atomic view of properties typically studied in condensed-matter experiments. This can help discern which features observed in condensed-phase experiments are already present in the gas phase; this information could be crucial as physicists attempt to understand surface magnetism, for instance.

2.2.2 Molecular "Structure-Reactivity" Relationships: High-Resolution Core-Level Electron Spectroscopy

Prediction of the chemical properties of molecular systems remains a "holy grail" of chemical physics. Recent advances at the ALS have brought us tantalizingly close to achieving this goal of inferring chemical properties (including reactivity) from high-resolution photoelectron spectroscopy. Inner-shell photoelectron spectroscopy of a molecule probes the ability of a molecule to accept charge at a selected atomic site within that molecule. The shifts in the binding energies of atomic core electrons in different molecular environments, as observed in photoelectron spectra, relate quite directly to properties that control fundamental chemical phenomena, such as acidity, basicity, rates of chemical reactions, and the relative strength of different competing chemical-reaction channels. Studies using high-resolution electron spectroscopy have literally generated a demonstrably deeper understanding of these phenomena. The capabilities of the ALS permit us to explore all implications of this link between spectroscopy and chemical behavior, in previously unimaginable detail.

Broad application of inner-shell electron spectroscopy to extract chemical insights has been frustrated by the fact that much interesting chemistry involves carbon atoms with very different chemical properties but similar ionization energies. An example is propyne (CH_3CCH) in which the range of carbon-1s ionization energies spans less than 2 eV; but remarkably, the reactivities of the three carbon atoms in this molecule differ significantly. Recent experiments at the MAX Lab at the University of Lund in Sweden and the ALS have made a major contribution that was hitherto

impossible: one can now resolve the different roles of the three inequivalent carbons as can be seen in Figure 1 (data taken at the ALS). Analysis of the measured ionization energies has generated a new view of the factors affecting chemical reactivity. A number of further investigations are expected to deeply affect our views of chemical processes at a fundamental level, with many conceivable applications. The ALS with its brightness and resolution in the low-photon-energy range, is presently, the only light source in the world where these experiments can be performed.

2.2.3 Ion- and Electron-Imaging Spectroscopies

Understanding the multibody breakup of a many-component atomic or molecular system when energy and momentum is imparted to the system by a single photon is one of the most basic problems in atomic-collision physics and chemical dynamics. The forces involved are well known, but the manner in which components react to these forces remains inadequately understood. Cold-target recoil-ion momentum spectroscopy (COLTRIMS) unravels the dynamics of a multiparticle ionization and/or dissociation process stimulated by photoionization of an atom or molecule. This method at the ALS has made it practical to construct a comprehensive map of the entire correlated final-momentum space without having to choose *a priori* particular angles or energies of one or more of the particles. The data can of course be presented in any appropriate set of coordinates (e.g., Jacobi or hyperspherical coordinates) that help to emphasize the key interactions or collective motions of components in the system. Finally, advances in visual presentation of the data immediately invite the identification of dominant ionization and dissociation mechanisms. The photon energies required are those that couple to the electronic motion of the target, precisely the UV and soft x-ray regions for which the ALS is optimized. The intensity of the ALS is critical for a successful measurement of these comparatively weak fragmentation channels. Moreover, the momentum resolution of the COLTRIMS imaging technique relies on the small spot sizes permitted by the high brightness of this third-generation light source.

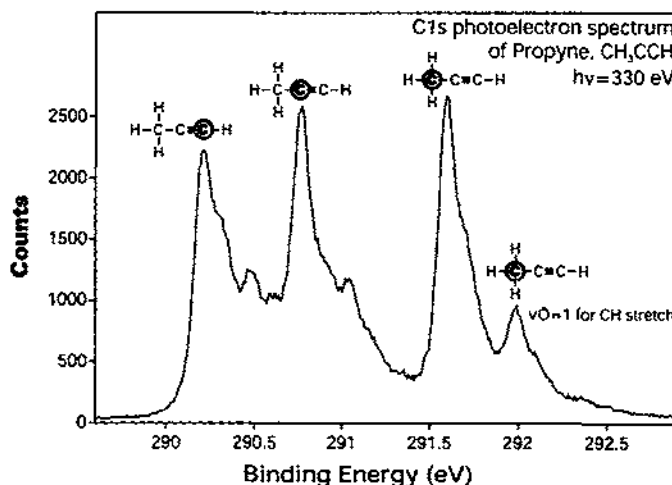


Figure 1. The carbon-1s photoelectron spectrum of propyne, CH_3CCH , measured using 330-eV photons from the Atomic, Molecular, and Optical Physics Beamline (undulator Beamline 9.0.1) at the ALS. Contributions from the three chemically inequivalent carbons in the molecule are well resolved and indicated on the figure. The ability to selectively probe individual carbon atoms within a molecule will lead to a greater understanding of chemical reactivities at the most fundamental level. [Figure courtesy of D. Thomas, Oregon State University, et al.]

Similar imaging techniques used for the energy- and angle-resolved study of photofragmentation of large molecules have provided dynamical information about the fragmentation process, such as bond-specific dissociation. These types of multi-differential studies, limited at second-generation facilities, can provide information on photochemistry induced by inner-shell ionization and multi-charged ion potentials when used at bright sources like the ALS.

2.2.4 Structure and Dynamics of Atoms and Molecules

2.2.4.1 Auger Resonant-Raman Spectroscopy

Understanding Auger decay processes induced by removal of an inner-shell electron in an atom or a molecule is a fundamental scientific issue. The challenge arises because it is generally impossible to resolve all Auger transitions, regardless of experimental resolving power, especially in molecules where vibrational and rotational substructure add complexity. This limitation derives from the fact that natural line widths associated with inner-shell ionization processes can be greater than the separation of subsequent Auger transitions, making them unobservable directly. However, the use of a narrow-bandwidth photon source, such as the ALS, in conjunction with a high-resolution electron-energy analyzer allows this limitation to be bypassed through Auger resonant-Raman measurements (discrete excitation of an inner-shell electron to a specific excited state). In this case, the natural width of the core-excited state does not determine the width of the Auger electron lines; it is controlled by the natural width of the final state alone. Since this can be negligible compared to the width associated with the core hole, Auger resonant-Raman spectroscopy (ARRS) measurements are essentially limited only by experimental factors (photon- and electron-energy resolutions). These types of measurements are thus perfectly matched for the high resolution achievable at the ALS and produce a clearer picture of inner-shell processes with a new level of detail.

For example, the vibrational progressions for molecular Auger decay can be completely resolved and mapped with unprecedented accuracy as can be seen in Figure 2 in the case of the $1s$ excitation of

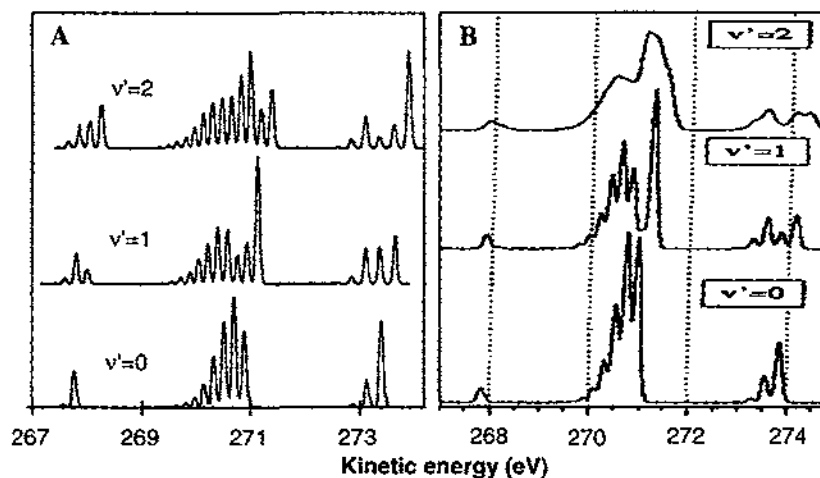


Figure 2. Decay spectra of the carbon $1s \rightarrow \pi^*$ resonance in the CO molecule. A shows spectra recently measured at the ALS. B shows calculated spectra convoluted to match the spectra measured at the National Synchrotron Light Source (NSLS). [Figure A taken from M.N. Piancastelli et al., *J. Phys. B* **30** (1997) 5677; Figure B courtesy of E. Kukk and N. Berrah, Western Michigan University, and J. Bozek, LBNL.]

CO to the molecular π^* orbital (measured recently at the ALS). These results are used to derive accurate shapes for the potential-energy curves. When coupled with imaging measurements, ARRS becomes an excellent tool for studying molecular photodissociation and other dynamic processes where the time scale of the nuclear motion is comparable with the lifetime of the core hole, in addition to discrete excitation to Rydberg series and post-collision interaction effects. It is also possible to adjust this tool by detuning the exciting photon energy from nominal resonance energy, thus decreasing the average decay time of the core-excited state. This experimental method that takes full advantage of high-resolution undulator beamlines of the ALS has the potential to allow the observation of new structure that could be associated with new physics.

2.2.4.2 Soft X-Ray Emission Spectroscopy

Pioneering work at second-generation light sources demonstrated that soft x-ray emission from gas-phase molecules following selective excitation probes their electronic structure and their nuclear geometry sensitively. The difference between selection rules for photon-in/photon-out spectroscopy and photoemission suggests that the two-photon experiments probe electronic structure in a manner complementary to electron spectroscopy. The angular-momentum character of molecular states, for instance, can be easier to discern from soft x-ray emission. In addition, the advantages of sub-natural-linewidth resonant-Raman studies presented above apply equally well to resonant photon emission (resonant inelastic scattering), as has been demonstrated in initial work at the ALS.

Extension to larger molecules, perhaps of biological, chemical synthetic, or pharmacological importance, could be feasible in some cases. The high penetrability of soft x rays in low-Z substances like air and water raises the possibility that species can be studied in realistic ("dirty") environments. Beyond the immediate AMO scientific interest in sorting out intermolecular interactions in real systems, such studies additionally provide a deeper understanding of soft x-ray emission as a probe. This line of research thereby helps to improve the applicability of this diagnostic to other fields like molecular environmental science and catalysis.

2.2.5 Probing the Limits of Fundamental Approximations in Photoionization

Some of the standard approximations typically adopted for theoretical calculations of atomic and molecular photoprocesses are known to have limitations that require caution. The high flux and brightness available at the ALS permit new tests of these limitations. The most common assumption is the independent-particle approximation (IPA), a picture that neglects electron-electron correlations. While some spectacular failures of the IPA are well-documented in low-energy valence-shell photophysics, the IPA has often been taken for granted in the soft x-ray region, far from all thresholds. The XAMS (x-ray atomic and molecular science) group at the ALS has proven this notion incorrect for ejection of an electron from a non-S-subshell at high energies, which serves as an important warning to theorists.

Also commonly used in photoelectron spectroscopy is the dipole approximation, in which the scalar product of the light wavevector with the electron-position vector is assumed to be much less than unity; equivalently, the relevant electron-nucleus distances are assumed to be far smaller than the wavelength of the ionizing radiation. Measurements of soft x-ray atomic photoemission conducted at the ALS exhibit significant nondipole effects in the electron angular distribution. Even more striking and surprising, results have been observed for molecular species. The limitations of these standard "textbook" approximations deserve further study to delimit the extent of their failures.

2.3 Strongly Correlated Systems

Modern theoretical quandaries in atomic, molecular, and optical physics revolve around systems for which the independent-electron approximation fails qualitatively. In this sense, AMO theory faces many of the same difficulties as other fields, such as high- T_c superconductivity. Even such seemingly simple processes as two-electron photoionization of the lightest atomic species (He, H^-), using VUV photons, have proven to be a formidable challenge, owing to our limited understanding of the three-body continuum states of three charged particles. The “accepted value,” as recently as five years ago, of the peak double-photoionization cross section for helium turned out to overestimate the correct result by more than 25%. A rich variety of two-electron excited-state resonances also exist in helium, in which the electrons move jointly as a correlated pair. The high intensity of the ALS in the VUV and soft x-ray ranges, combined with a detection technique that measures the three-dimensional momentum vectors of all particles after double photoionization, has recently allowed advances in the understanding of the dynamics of this few-body breakup.

An intellectual challenge that remains to be understood for helium is: “Where is the chaos?” The classical dynamics of the helium electrons is chaotic at all energies, yet the low-lying bound and doubly excited autoionizing states exhibit striking regularities that have been the subject of intense study and interpretation dating back to the 1960s. Recent theories have suggested that regimes should exist closer to the double-ionization threshold in which so many resonances overlap that a new spectral regime of “quantum chaos” should emerge. To test these ideas in helium (or the isoelectronic species H^- or Li^+), i.e., to map out the chaos while searching for simplicity and regularity in the spectrum as well, will require the extremely high resolution and brightness of a third-generation source like the ALS. (Note that extensive laser-based experiments have been carried out for other “two-electron systems,” such as barium, but the breaking of the $O(4)$ symmetry in any nonhydrogenic ionic core changes the problem fundamentally, as compared to true two-electron species.)

Another challenge to be overcome for few-body systems is the interpretation of the rich multichannel spectroscopy of triply excited hollow atoms, of which lithium is the prototype. The high spectral resolution achieved at the undulator beamlines of the ALS sparked a very recent breakthrough in which several new hollow states of atomic lithium were measured. These data provided a much-needed confirmation of recent improvements in theoretical methods, as shown in Figure 3. These systems critically challenge theory, which ultimately leads to their quantitative improvement and hones our qualitative understanding. Many intricacies remain to be measured and interpreted.

Progress in these areas is contingent on close cooperation between theory and experiment. The bottom line is that, despite the rapid progress in theory during the past decade, the description of triply and doubly excited states in all light atoms (and negative ions) of the periodic table remains far from routine. Only for energies near the lowest ionization thresholds can the theory be viewed as being basically under control. Experiments at the ALS are perfectly poised to contribute to the improvement of some of the key remaining gaps in theoretical descriptions.

The areas just mentioned relate to problems where our fundamental understanding of the basic processes is still unsatisfactory. Consumers of atomic data (e.g., the plasma modelers) bring a different perspective to these matters, owing to the great number of cross sections needed, which makes it impossible to rely entirely on experiments for every number. Theory must ultimately provide this data, yet, as discussed above, there remains a need for benchmark tests that are sufficiently broad in number and variety to ensure that reliable theoretical methods exist to describe the broad array of photoprocesses that exist in the periodic table.

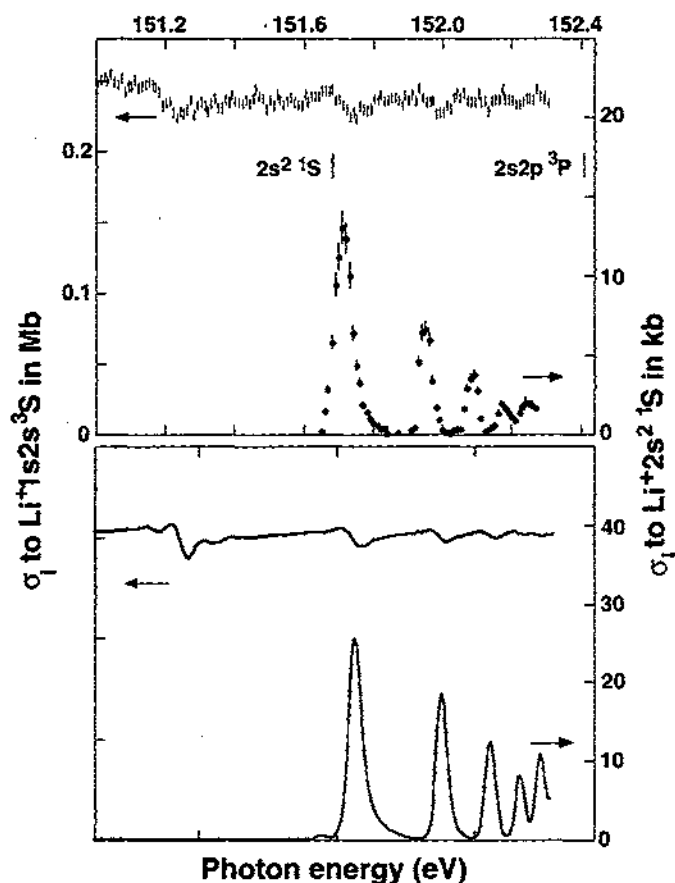


Figure 3. High-resolution spectra over the excitation-energy range of the $[(2s2p^3P)ns]^2P$ Rydberg series. The upper panel shows the measured values of partial cross sections for photoionization of $1s^22s^2S$ lithium atoms into $1s2s^3S$ (lower curve, right scale) Li^+ ionic states. The lower panel shows the results of convoluted R -matrix calculations for the same partial cross sections as in the upper panel. [Figure courtesy of François Wuilleumier and Denis Cubaynes, Université de Paris-Sud.]

2.4 Photofragmentation Control: Tailored Excitation and Detection of Atomic and Molecular Systems

A long-standing goal in AMO physics is to achieve maximal control of processes all the way down to the molecular and even atomic levels. The areas described below are directed, in the long run, toward achieving this control and toward extracting the deeper understanding of complicated processes that must be achieved before such control will be feasible.

2.4.1 Laser-Tailored Initial States

The high brightness of the ALS significantly enhances our ability to perform a broad class of experiments in which either the sample or the photofragment detection is tailored in a specific manner. One example is the use of a laser to prepare an oriented or aligned atom by laser-optical pumping,

after which a synchrotron photon ionizes an inner shell of the atom. For example, recent measurements of dichroism in transition-metal atoms have dramatized the inadequacy of the independent-particle model, which is commonly used in condensed-matter calculations, in situations where the core level is split by an effective spin field. Gas-phase atomic studies have demonstrated a strong interaction between the 3p hole and the 3d electrons, which was neglected in past theoretical work. Such studies can pinpoint the role of intra-atomic interactions in spectra of metal surfaces and thin metal films, thereby providing insight into magnetic materials and thin films. The AMO community contributes to our understanding of these problems by disentangling the role of intra-atomic and inter-atomic interactions.

A different use of laser-prepared initial states is exemplified by the planned improvement in resolution through the optical pumping of trapped atoms, which will give a far better measurement of lithium double photoionization, for example. Owing to the tenuous nature of the targets, however, it may be necessary to wait for the arrival of free-electron lasers (FELs) to carry out these experiments.

Although it has not yet been achieved, the prospect of coupling infrared (IR) lasers and synchrotron radiation to study inner-shell excitation of vibrationally excited molecules is extremely appealing. For example, an experiment of this type could be used to probe the dependence of inner-shell processes on the internuclear distance, which translates directly into new insights that bear on the nature of chemical bonding and electron correlation. Another challenge for theory occurs when a molecular target is prepared in a very high vibrational state near the dissociation limit and then photoionized. A key benefit of such experiments is the information they reveal concerning poorly mapped parts of the potential-surface manifolds far away from the ground-state Franck-Condon zone. The simple combination of a cw laser with a synchrotron source permits the photoionization of an electronically excited atom, which exhibits rich and informative spectral dynamics that usually differ qualitatively from ground-state photoionization. Early experiments of this type were performed with second generation sources and, in the case of hollow atomic lithium, were improved in a clear and qualitative manner when reexamined recently at the ALS.

This work lays the foundation for future studies in which laser excitation is used to tailor the atomic or molecular configuration in order to enhance a particular interaction or decay process that is subsequently probed by inner-shell excitation. An immediate extension of these techniques, a pulsed laser that is synchronized with electron bunches (of 40-ps bunch length) in the ALS storage ring opens the possibility of a new class of experiments. In these, the laser labels the species of interest and the synchrotron is used to probe it. Such double-resonance experiments can selectively study a minor component (e.g., a free radical, ion, or size-selected cluster) of a complex mixture, a common desire for many types of samples.

2.4.2 Molecular Studies with Lasers and Synchrotron Radiation: Multicolor Experiments

Although multiphoton spectroscopic techniques are widely used in laboratory laser experiments, the combination with synchrotron radiation brings a new perspective. For example, molecular photon-induced dissociation by two-color experiments (combination of infrared, visible, ultraviolet or soft x-ray photons) can be achieved in a variety of "pump-probe" arrangement where one photon either photodissociates or photoexcites the molecule, while the second photon photoionizes or photoexcites the fragments or the excited target molecule. In addition, pulsed photon sources combined with an appropriate pulsed laser can be employed in time-resolved experiments. Since second-generation

synchrotron-radiation sources could only achieve limited spectral resolution and focusing capabilities, third-generation sources like the ALS will permit significant improvements in several areas, as long as the storage ring operates in few-bunch mode to allow a large dynamical range for the pump-probe delay time.

Photodissociation experiments using double-resonance or pump-probe techniques generally fall into one of two different categories. In the first, molecular photodissociation of suitable precursor molecules is used to provide a clean and efficient source of free radicals (species with unpaired electrons), which can then be characterized by using the full range of VUV and soft x-ray techniques. In this case, the laser is used for the photodissociation step and the synchrotron radiation is used as the probe. In the second category, the photodissociation process is itself the object of study, and the product yields, angular distributions, velocity distributions, etc. are determined as a function of the photodissociation wavelength. In some instances, photoionization mass spectrometry using the synchrotron will be used as a universal detector of the products of photodissociation dynamics initiated by the laser. This scheme will be particularly useful for the detection of radical fragments that are not well characterized spectroscopically. In other instances, laser-based techniques will be used to probe the molecular explosion that often follows inner-shell ionization with the VUV or soft x rays from the synchrotron. Extraction of the dynamical information from this process requires knowledge of the energy content and distribution (electronic, vibrational, and rotational) among the fragments. The large number of competing dissociation channels forces the use of a highly selective and sensitive probe like laser-induced fluorescence. The three-body dissociation of valence-excited molecules poses extraordinary challenges as well, because the dissociation could proceed through a cascade of two-body dissociations or through a concerted three-body process. Analogously, molecular ions (singly or doubly charged) produced by autoionization exhibit peculiar fragmentation signatures, caused in some cases by atomic scrambling (bond breakage and new bond formation).

For time-resolved experiments, synchronization of the two sources is necessary whenever the lifetime of the excited species is less than the temporal separation of the light pulses. High-repetition-rate Q-switched, mode-locked dye lasers are the most suitable. A free-electron laser built in a straight section of a third-generation storage ring can provide tunable light from the IR to the UV, and by harmonic generation to the VUV, with a high peak power that is naturally synchronized with synchrotron radiation produced by the same machine. Some of the scientific questions that can be addressed relate to "chemistry in the time domain," a topic discussed in the report of the Working Group on Chemical Dynamics.

2.4.3 Propensities for Final-State-Energy and Angular-Momentum Sharing

A fundamental scientific issue having broad interest and significance is the description of how the conserved quantities of energy, angular momentum, and linear momentum are dynamically shared and partitioned among constituent particles in an isolated-multiparticle atomic or molecular system. The quantification of this sharing and partitioning helps to unravel the nature of final-state interactions. These interactions control the extent to which the quantum states of two particles are coupled inseparably; such coupling is frequently denoted generically as a "correlation effect." In addition to their intrinsic interest as fundamental dynamic processes at the quantum level, the understanding of such correlations is also important in a broad sense because they arise in any quantum-mechanical system having nonseparable degrees of freedom. Such systems can involve so many fragmentation channels that they appear to be theoretically intractable at first sight. This makes the search for propensities and trends for the dominant pathways even more important than in systems that can be treated by *ab-initio* theory with a high probability of success.

As one example, measurements of high-resolution photoelectron spectra and/or photoelectron angular distributions directly provide the predominant resonance-decay pathways. In favorable cases, experiments of this type yield state-to-state propensity rules for the electron-ion collision (or half-collision) process; they can also identify the mechanisms that control the allotment of energy and angular momentum among the myriad photofragment degrees of freedom. In some cases, this information even bears on a question of longstanding chemical importance: how the motion of light electrons can influence the behavior of heavy nuclei. Measurements of anisotropic observables also test theoretical approximation schemes far more critically than studies of total cross sections.

Next on the scale of increasing complexity are circular-dichroism and optical-activity effects in molecular photoionization, which have received little attention and remains poorly understood. Circular dichroism in photoionization has not been observed for molecular targets, although it has received some theoretical attention dating back to the early 1980s. Particularly for chiral molecules, where orientation of the target is not required, such effects have potential importance for biological problems, e.g., the origins of biological homochirality, as well as for the basic physics of photoionization. The photoionization dynamics can be addressed with unprecedented detail if the photoelectrons are also spin-analyzed.

Despite the common conception, atoms and atomic ions are typically *not* spherically symmetrical. The anisotropy of ionic photofragments can now be explored in complex spectral regions characterized by rich resonance physics. Recent measurements at the ALS of interactions between an autoionizing *ns* Rydberg electron and an excited Ar^+ photofragment press theory to its current limits, while still showing signs of tantalizing simplicity in some regards. In the future, experiments with circularly polarized light will permit a more complete determination of the angular-momentum distribution in the ionic fragment. If a photoelectron is also detected at a specific ejection angle in coincidence with a fluorescence photon, probability amplitudes of the photoelectron emerge, as well.

2.5 Free Clusters: Site-Specific Inner-Shell Excitation

The domain of free clusters covers aggregates of atoms or molecules in numbers that vary from several to several thousand. One goal is to ascertain how the condensed-matter properties emerge as the number of atoms or molecules increases. Another aim is to search for specific properties of these mesoscopic objects that could be important in related fields, such as new molecules like the fullerenes, nanostructured materials, and specific chemical reactivities.

Pressing technological questions that can be addressed through the study of clusters include the ever-present demand to miniaturize microelectronic circuits, which necessitates a thorough understanding of cluster properties. Metal pads used to join layers of semiconductors are shrinking to the size where only a few thousand atoms of the metal are used. In this regime the metal behaves more like a cluster than a bulk metal. The formation of clusters in deposition processes also requires deeper understanding at the fundamental level in order to prevent contamination of the surface by large clusters, which can cause a device to fail. Two main directions are to be distinguished, one concerning atomic clusters, particularly metallic clusters, and the other concerning molecular clusters.

2.5.1 Atomic Clusters

Even the most refractory materials can now be produced in a very large range of sizes. In divalent metals, for example, it has been possible to observe the transition from an insulator to a metallic structure in which electrons are delocalized and described with a nascent band structure. Collective excitations are signalled by the presence of giant resonances. Photoionization studies (including

partial ion yields, photoelectron spectroscopy, or fragmentation) are fruitful in either the valence or core-level regions. The challenge is to perform such measurements for one size population of free clusters and track one property as a function of size. The low density of single-size-particles, probably in the $10^7/\text{cm}^3$ range, requires an extremely bright and intense photon source like an ALS undulator. Extended x-ray absorption fine structure spectroscopy (EXAFS) is an ideal tool to extract bond distances in amorphous species or nanocrystals.

2.5.2 Molecular Clusters

Homogenous or heterogeneous molecular clusters can mimic a microsolution. Detailed studies help to sort out the extent to which solvation affects the properties of a molecule. One intriguing area is the investigation of geometrical structure of positively or negatively charged clusters above a certain critical size. One problem that complicates the analysis is the coexistence of isomers in the cluster source. Ultimately, double-resonance experiments in which a mass-selected cluster is first labeled, then probed, will eliminate this difficulty. High-resolution pulsed-field-ionization zero-kinetic-energy (ZEKE) spectroscopy can also help to reduce this complexity. Finally, EXAFS near selected core levels is also attractive and, in highly-focused conditions, is the ideal tool to solve such problems.

3. Importance of VUV and Soft X Rays and the Role of the ALS

3.1 Why a VUV/Soft X-Ray Source Is Important for the Proposed Areas of Study

The scientific issues identified in this report require energy in the range for which the ALS is optimized, namely, the VUV and soft x-ray region. The broad and rapid tunability of the ALS in these photon-energy regions enables systematic studies of sequences of atoms and molecules that are inaccessible to even state-of-the-art laser systems. While such systematic studies have always been integral to AMO research, the unprecedented brightness of the ALS combined with the state-of-the-art beamlines and detection methods only now permits the study of large classes of highly rarified species, such as ions, open-shell atoms, and free radicals, and provides a level of detail that was only imagined in the past. Examples of such systematic studies, discussed in the report, include (1) inner-shell excitation; (2) determination of accurate photoabsorption and photoionization cross sections along isoelectronic sequences of atoms and multiply charged ions; (3) use of site-specific, inner-shell excitation to explore chemical reactivity in sequences within different classes of functionalized molecules; and (4) triply differential studies of open-shell elements where wavelength-dependent partial cross sections and angular distributions are measured simultaneously. We emphasize that the *science* is driving the selection of the light source for these experiments, rather than the reverse. Essentially, there are no other methods that are capable of achieving the scientific goals described in Section 2 above.

3.2 What Is the Role of the ALS?

Given the requirement of photons in the VUV/soft x-ray energy range, the question remains whether the proposed scientific programs are contingent upon the advanced capabilities of the ALS. Our answer is emphatically affirmative, as the technical case for this requirement is quite clear. Most of the experiments require *ultrahigh resolution, brightness (small spot size), and very high flux over a broad photon-energy range*. Only a source with the characteristics of the ALS is suitable for such studies. For example, high-resolution inner-shell atomic and molecular experiments using Auger resonant-Raman

or x-ray emission spectroscopy benefit directly from the availability of *bright, narrow-bandwidth, intense excitation*. High-resolution spectrometers, coupled with high-resolution photons, open the door to the investigation of the structure and dynamics of various atoms and molecules with high and revealing precision. These characteristics are also ideal for studies of ionic photoexcitation and photoionization. Although ion beams provide a sparse target for such studies, pioneering experiments have been successfully conducted in Europe and Japan at second-generation synchrotron-radiation facilities, demonstrating their viability and scientific potential. In general, however, these experiments have been limited to species with enormous cross sections. The increased photon flux of the ALS provides a unique opportunity to conduct such studies now with dramatically increased precision, spectral resolution, and variety of ion targets. Such studies have *never* been attempted for negative-ion targets, for example, and offer an exciting opportunity for pioneering experiments.

Another area for which the ALS is uniquely capable is in the area of spin-resolved experiments that require *intense circularly polarized light*. This important resource will be provided by the elliptically polarized undulator (EPU) beamline presently under construction.

3.3 What Tools Are Needed?

In order to measure atomic and molecular processes after photoionization, tools are required for preparing atomic and molecular samples, including ions in specific states, for exciting them, and for detecting the fragments. Two dedicated beamlines (a bend-magnet beamline and an undulator beamline) are being used for AMO research in conjunction with several state-of-the-art end stations that include an ion beamline for study of ion-photon interactions (in construction), high-resolution electron spectrometers (time-of-flight spectrometers, hemispherical analyzers), fluorescence detectors, ion detectors and provisions for a variety of coincidence techniques (e.g., photoelectron photoion coincidence (PEPICO), photoion-photoion coincidence (PIPICO), and COLTRIMS).

Other tools are, however, needed in order to “prepare” and “control” atomic and molecular targets or to otherwise extend experimental capabilities. These are:

- (1) Mott-detectors for spin-polarized detection.
- (2) Pulsed lasers to prepare targets and to synchronize them to the ALS for time-resolved studies.
- (3) Extend the spectral range of the EPU beamline to cover low photon energies. The ALS management has stopped the development of the second undulator (which would have provided low photon energies) on the *only* elliptically polarized beamline of the ALS.
- (4) A branch of an undulator beamline without a monochromator that is capable of running in a “blowtorch mode” in order to provide ultimate intensity for a certain class of experiments that need flux far more desperately than resolution. For example, all experiments that require a high degree of differentiation, such as angle- and/or spin-resolved measurements, electron-electron and electron-ion coincidence measurements, and spectroscopy of polarized targets, are in need of optimum high flux because the count rates are extremely low.
- (5) An undulator beamline that covers the oxygen and nitrogen edges with very high brightness and resolution.
- (6) Timing operation is absolutely necessary for several types of experimental techniques (time-of-flight techniques). The ALS must be committed to serving the AMO community, which depends upon that mode of operation.

(7) UV and IR free-electron lasers are the next-generation sources, and are particularly promising for double-resonance experiments. The ALS management is encouraged to pursue that area of development.

4. Connections to Other Fields

AMO science has a strong track record as an enabling science for other disciplines. The benefits of understanding the underlying atomic and molecular physics occurring in photoexcitation and photoionization have applications in several other fields, including biology, atmospheric physics, astrochemistry, radiation damage of molecules, environmental science, lasers, astrophysics, fusion plasma physics, material and surface sciences, and chemical manufacturing.

Studies of the properties of ions are needed since the production and destruction of negative ions in systems such as dilute plasmas appearing in the outer atmospheres of stars are strongly affected by the characteristics of these ions. The proposed studies of highly charged ions are relevant to the development of novel x-ray laser configurations whose lasing medium is a plasma. Information on ions is also important for the low-energy plasmas used in materials processing, plasma etching, and other industrial applications. Finally, the development of new experimental techniques could lead in the longer term to the manufacture of novel detectors and electronics, as was the case in the past for time-of-flight spectrometers and imaging techniques.

VUV studies are also relevant to questions regarding global climate change. For example, the large-scale industrial consumption of chlorofluorocarbons (CFCs) has attracted a lot of attention because of their destructive effects on atmospheric ozone and global change. Since the Montreal Protocol a decade ago, many industries are attempting to replace traditional CFC-based products (the so-called Annex A and B controlled substances), including refrigerants, aerosol propellants, plasma etchants, etc., with more environment-friendly substitutes, which consist primarily of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and their derivatives. The ALS has photon beams well-suited to systematic studies examining the photoexcitation of a series of common substitutes, including HCFCs and HFCs. Comprehensive photoabsorption and photofragmentation cross sections are needed to detail the response of these molecules to photons in the VUV and soft-x-ray regions. Characteristic photoion-photoion coincidence (PIPICO) spectra can not only map out the dynamics of a dissociation process that follows photoexcitation, but it can also provide an element-specific fingerprint of the target of interest by tuning the excitation photon energy to specific ionization edges. This type of photodissociation information could be used ultimately to diagnose unknown waste emission or for other smog analysis.

In addition to potential practical relevance, photoabsorption and photofragmentation measurements of HCFCs and HFCs can provide important insight to shape-resonance phenomena and non-Franck-Condon behavior in relatively large molecules and can aid in critically evaluating photoionization theories and electronic-structure calculations. Experiments feasible at the ALS offer the first comprehensive research on photodissociation of these complex molecules, and they could impact areas such as environmental research, radiation and space sciences, fusion research, aeronomy, and astrophysics.

Absorption spectroscopies using the ALS can provide element-specific and chemical-state-specific detection of trace contaminants in soils, groundwater, and biological materials. The spectroscopy methods can be applied to understand radiation damage in complex biological molecules, since a thorough understanding can only be done through studies of the decay processes after photoionization.

The development of high-resolution, sub-natural linewidth spectroscopies, such as resonant-Raman and resonant-Raman Auger techniques, may ultimately have considerable utility in more applied areas of VUV and soft x-ray physics. For example, traditional near-edge x-ray absorption fine structure (NEXAFS, also known as XANES) spectroscopy has commonly been used to determine the oxidation state of selected elements in environmental and biological samples. For many elements, however, the NEXAFS spectra for different oxidation states are quite similar, and the analysis of samples with mixed oxidation states can be extremely difficult. The increased spectral resolution afforded by resonant-Raman and resonant-Raman Auger spectroscopy promises to improve and simplify such analyses. Ultimately, the development of such new spectroscopies in AMO physics is expected to enable a broad range of new capabilities in the environmental and biological sciences.

5. Conclusions

First- and second-generation synchrotron-radiation sources have been pioneering tools for several areas of atomic and molecular research. They generated new understanding and paved the way to future high-precision and highly differential investigations of the structure and dynamics of atoms and molecules. This future has arrived. Synchrotron-based AMO physics research conducted with the third-generation ALS has already provided a new understanding of basic photon-matter interactions in a number of different systems. These synchrotron research projects provide broad training to large numbers of undergraduate and graduate students, who contribute in turn to other research fields and to industry. First and foremost, however, an enthusiastic community of atomic, molecular, and optical scientists is committed to advancing, with a sense of urgency, the exciting scientific frontiers stimulated by the construction of the ALS.

Working Group on Chemical Dynamics

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1. Introduction

The field of chemical dynamics studies the elementary chemical reactions that underlie virtually all macroscopic chemical systems. It is a strongly coupled experimental-theoretical effort that can provide a solid foundation for understanding the gas-phase chemical processes on which predictive models of combustion and atmospheric chemistry must rely. The objective of this section is to identify exciting opportunities for chemical dynamics and to investigate how the Advanced Light Source (ALS) can help in achieving the scientific goals. Tremendous advances in the areas of lasers and molecular beams have already made a substantial impact in this field, but the unique features of the ALS make it possible to solve a number of previously unreachable problems in the following key areas:

- Combustion: Radical Chemistry and Dynamics.
- New Molecules.
- Atmospheric Chemistry and Global Change.
- Astrochemistry.
- Clusters/Interfacial Chemistry.
- Plasma Chemistry.
- Chemistry in Real Time.
- Photoionization Dynamics of Complex Molecules.

The Chemical Dynamics Beamline (Beamline 9.0.2) at the ALS represents a unique facility, the first in the world to combine dedicated, intense undulator radiation with state-of-the-art molecular-beam machines for a broad range of studies of fundamental chemical processes. The beamline achieved full operation in November 1995 with the installation and commissioning of the U10 undulator, which

is the world's most intense source of continuously tunable vacuum-ultraviolet (VUV) light. The scientific promise afforded by the new Chemical Dynamics Beamline is now just beginning to be realized. A report ["Application of Synchrotron Radiation in Chemical Dynamics," P. Heimann, M. Koike, A. H. Kung, C. Y. Ng, M. G. White, and A. Wodtke, LBL-34131, May 1993] outlined the initial goals of the program. Many of the milestones mentioned in that report have been achieved as the scientific program has begun in earnest and as outside users have come to Berkeley to take advantage of the facility. The end stations are now fully operational, the normal-incidence monochromator has demonstrated world-record resolution, and breakthroughs have been achieved in photoionization studies, photochemistry, and, recently, crossed-beam reactive scattering. Visitors have come from Cornell University, Brookhaven National Laboratory, the University of North Carolina, the University of Waterloo, Purdue University, State University of New York at Stony Brook, and University of California, Davis to take advantage of the facility, and the user base is ramping up rapidly. The scientific advances recently achieved and the promising future directions are outlined below.

2. Opportunities in Chemical Dynamics

2.1 Combustion: Radical Chemistry and Dynamics

Despite the short time since it has come on line, the end stations at the Chemical Dynamics Beamline have already begun to have a significant effect on our understanding of combustion chemistry. The high flux of the ALS available at the crossed-molecular-beam end station has allowed sensitive universal detection of reaction products, while the tunability of the ALS has been used to discriminate among competing product channels. The high resolution available from use of the Eagle monochromator has opened the door to a new generation of studies on the photoelectron spectroscopy of radicals. Future developments can extend the techniques available for exploration of new systems. The subsections below describe some recent work and future directions.

2.1.1 Reaction of Radicals with Hydrocarbons

Crossed-beam reactions of halogen atoms with saturated hydrocarbon molecules have recently been investigated by the Suits group using soft-VUV ionization for direct measurement of the hydrocarbon-radical fragment for the first time. Radical abstraction of primary or secondary hydrogen atoms from hydrocarbon molecules represents a crucial aspect of the dynamics of these reactions, important for developing a predictive understanding of combustion systems. The crossed-beam reaction of chlorine with propane showed clear energy-dependent dynamics indicating abstraction of secondary hydrogen atoms that led to forward-scattered, internally cold propyl radicals. The backscattered component, which moved to sideways scattering at higher collision energy, indicated reaction of the primary hydrogen atoms was mediated by an entrance barrier. Reaction with n-pentane showed similar behavior with one striking difference: the forward-scattered product was unambiguously the 2-pentyl radical, which was formed even colder than in the propyl case. The backscattered pentyl radicals, however, showed a translational-energy release nearly 1 eV lower than the forward-scattered products, dramatically showing the involvement of the carbon skeleton in the collision. Past studies of these reactions have relied on state-resolved laser probing of the HCl product, with the assumption of uncoupled energy and angular distributions being used to allow reconstruction of the differential cross sections, an assumption we see is of limited validity. The laser experiments are thus blind to these key aspects of the reaction. Universal probing of the radical fragment via undulator radiation allows the complete picture of the dynamics to emerge.

This work demonstrates that the crossed-molecular-beam end station is already having an impact on combustion dynamics. It should now be possible to investigate many other radical-molecule reactions with good detection sensitivity in a state-of-the art molecular-beam system.

2.1.2 Photodissociation of Hydrocarbons

The photodissociation and chemistry of hydrocarbons and related species is of considerable interest in modeling combustion processes. As the complexity of these species increases, however, they become less accessible to investigation by "standard" techniques. For example, state-resolved laser-based methods are rarely practical for probing hydrocarbon systems beyond CH_3 . Furthermore, in a conventional crossed-beam instrument with electron-impact ionization, product identification is greatly complicated by dissociative ionization of parent masses, and discrimination between different product isomers of the same mass is not possible. Using tunable VUV undulator radiation as a universal but selective probe, both of these issues can be addressed. Dissociative ionization can be prevented by tuning the photon energy below the onset of dissociation. Background interference is thus nearly eliminated. Furthermore, if two product isomers have different ionization potentials, as is often the case, they can be distinguished using tunable VUV ionization.

As an example, the Neumark group has investigated the photodissociation at 193 nm of allene (CH_2CCH_2) and propyne (CH_3CCH) on End Station One of the Chemical Dynamics Beamline. Both have the chemical formula C_3H_4 , and both undergo primary dissociation to $\text{C}_3\text{H}_3 + \text{H}$. However, the chemical identity of C_3H_3 is unclear; it could be the propargyl radical (CH_2CCH) or the propynyl radical (CH_3CC). One expects and finds exclusively the propargyl product from dissociation of allene, as shown in the upper panel of Figure 1, but either product is possible from dissociation of propyne. However, breaking the acetylenic bond in propyne takes 40 kcal/mol more energy. The two channels can be distinguished because their ionization potentials are quite different: 8.7 eV for propargyl and 10.8 eV for propynyl. As shown in the lower panel of the figure, there is significant dissociation of propyne to propynyl, indicating substantial bond-selectivity in which the stronger bond breaks.

Other recent examples are provided by the studies of Lee and co-workers on the photodissociation of dimethyl sulfoxide and of Hall and coworkers on acrylonitrile and vinyl chloride. As in the allene and propyne examples, complex, multichannel dissociations are analyzed by taking advantage of the fact that tunable ultraviolet ionization produces reduced cracking of the parent molecule and permits both selective detection of different species with the same mass and low-resolution spectroscopy of internal energies. Momentum matching has been exploited in the dissociation of these molecules to give quantitative dissociation energies and recombination barriers for radicals such as H_2CCl , H_2CCH , and CH_3SO . Future experiments can be optimized to investigate unimolecular decomposition and isomerization of energetic free radicals.

2.1.3 High-Resolution Molecular Photoionization

Recent developments at the high-resolution photoionization and photoelectron end station at the Chemical Dynamics Beamline of the ALS have made possible ultrahigh-resolution measurements using the photoionization, threshold photoelectron (TPE), and pulsed-field-ionization (PFI) zero-kinetic-energy photoelectron (ZEKE) spectroscopic techniques. Energetic and spectroscopic data for gaseous ions can now be measured routinely at resolutions of 2 cm^{-1} to 5 cm^{-1} using this facility, making it a unique apparatus for VUV photoionization and photoelectron studies of gaseous molecules in the photon-energy range of 6 eV to 27 eV. The energetic information for molecular ions

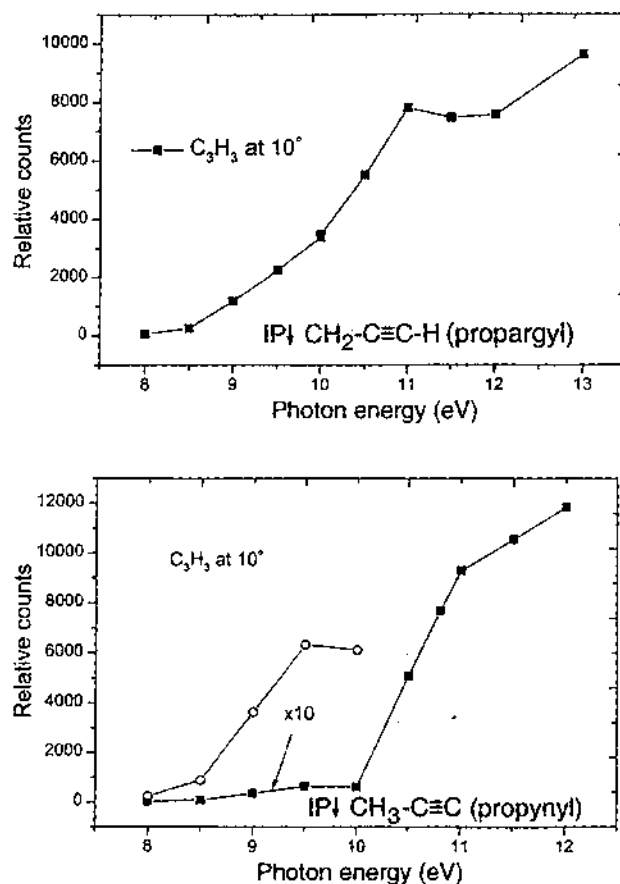


Figure 1. Hydrocarbon photodissociation at the ALS. Allene (top) and propyne (bottom) are photodissociated at 193 nm. The product scattered at various laboratory angles is ionized with VUV radiation and mass-analyzed. The figure shows the ionization efficiency of the mass-39 product at 10° (CH-bond fission) produced from both precursors. The product species clearly have different ionization potentials. The propargyl radical is produced from allene, and the propynyl radical is produced from propyne. The latter channel is particularly interesting since it represents dissociation of the much stronger (by 40 kcal/mol) C-H bond in propyne. [Figure courtesy of D. Neumark, University of California, Berkeley.]

thus obtained can be used in thermochemical cycles to derive highly accurate heats of formation, as well as dissociation energies for neutral molecules. Since accurate energetic and structural data for radicals are lacking in the literature, the photoionization and photoelectron capability of the Chemical Dynamics Beamline should play an important role in providing these data for key reactive intermediates relevant to combustion, plasma, atmospheric, and interstellar chemistry.

Rotationally resolved (or partially resolved) photoelectron spectra of small radical hydrides, e.g., CH, CH_2 , NH, NH_2 , HCO, CH_3O , and C_2H , are of particular interest because these species are important intermediates in combustion chemistry. Polyatomic hydrocarbon radicals are another class of intermediates relevant to combustion and planetary chemistry. Photoionization studies of polyatomic hydrocarbon radicals provide fundamental information about the vibrational excitation in hydrocarbon cations and about transitions from classical to nonclassical structures, e.g., bridged hydrogen in ethyl and propargyl cations.

Accurate energetic and spectroscopic data obtained for open-shell and highly correlated radical and ionic species also provide tests of state-of-the-art *ab-initio* calculations. High-resolution, rotationally resolved photoelectron measurements allow the testing of symmetry-selection rules and the angular-momentum balance involved in photoionization processes. These fundamental data, which can be obtained routinely in a high-resolution photoelectron experiment, can be used to elucidate cation geometries and vibronic couplings.

High-resolution photoelectron studies of polyatomic radicals will require the further development of radical sources. Many polyatomic radicals can be produced readily in electrical discharge, photodissociation, and thermal-pyrolysis. However, radicals thus formed often coexist with their precursors and with secondary reaction products. The photoelectron spectrum of a radical in a mixture of other species can be isolated with high sensitivity using the threshold photoelectron-photoion coincidence (TPEPICO) scheme.

Mass-selected threshold-ion (MATI) spectroscopy involves the detection of ions formed by the PFI of high-*n* Rydberg species. Preliminary efforts in the measurement of the MATI spectra for molecules at the Chemical Dynamics Beamline have been partially successful, and changes in the ion optics based on the experience gained in these preliminary studies are under way. Since MATI is a threshold-ionization technique, it provides the same spectroscopic capabilities as ZEKE, with the tremendous added advantage of clear identification of the species responsible for the spectrum. This mass labeling of the high-resolution photoelectron spectrum makes the MATI technique perfect for high-resolution photoelectron spectroscopic studies of radicals and clusters, which are usually prepared in a source coexisting with other impurities.

An entirely new type of threshold ionization spectroscopy, similar in spirit to ZEKE or MATI, has recently been demonstrated using coherent VUV light in the laboratories of John Hepburn of the University of Waterloo. This technique, called threshold ion-pair-production spectroscopy (TIPS), is based on the Rydberg-like behaviour of very high vibrational levels in ion-pair potentials. The existence of these levels means that one can make a very precise determination of the threshold for ion-pair formation using pulsed-field ionization with a MATI-type spectrometer. In fact, exactly the same ion optics are used for MATI and TIPS. Since TIPS determines the precise energetic threshold for $AB \rightarrow A^+ + B^-$ to an accuracy of 1 cm^{-1} , if the ionization efficiency of A is measured by ZEKE/MATI and the electron affinity of B is measured by precise ion-beam techniques, the TIPS result can determine the bond energy of neutral A-B to wavenumber accuracy, as has been demonstrated by Hepburn's group for O_2 , HF, and HCl. The broad tuning range and superior VUV flux at the Chemical Dynamics Beamline will allow for studies of polyatomic molecules, where frequently bond energies are not well known. Since ion-pair formation is a common process in molecules, TIPS should be widely applicable. Some examples of very interesting systems to study are CH_3F , CF_4 , and HCN. In addition, because TIPS is a spectroscopic technique, it can measure the spectrum of the molecular-ion fragment if the other ionic fragment is an atomic ion. For example, the TIPS spectrum of $HCC \rightarrow HCC^- + H^+$ will reveal the spectrum of the HCC^- anion, along with the dissociation energy of the $HCC-H$ bond. Because of the higher electric fields involved in typical applications of TIPS or MATI, the energy resolutions are usually on the order of 2 cm^{-1} to 4 cm^{-1} , making these two techniques perfectly suited for the Chemical Dynamics Beamline at the ALS. Because of the high flux and tuning range in the VUV, implementation of TIPS and MATI at the ALS is very important.

2.2 New Molecules, New Chemistry

The "soft-ionization" feature made available by the tunability of the ALS allows one to detect weakly bound molecular systems without fragmenting them. In addition, one-photon ionization is a universal probe requiring no prior spectroscopic information. This powerful combination of selectivity and universality makes it possible to detect and characterize new radicals and metastable molecules, as discussed in the next section.

2.2.1 New Radicals

The weakly bound radical product ClCO has been directly observed for the first time, using End Station One of the Chemical Dynamics Beamline and the undulator "white" beam. This radical is believed to play a critical role in combustion of halogen containing wastes and in the formation of photochemical smog. The use of soft ionization by tunable undulator radiation allowed for direct observation of this unstable radical and, for the first time, the measurement of its photoionization-efficiency curve (Figure 2). Other weakly bound or highly reactive radicals might similarly be investigated.

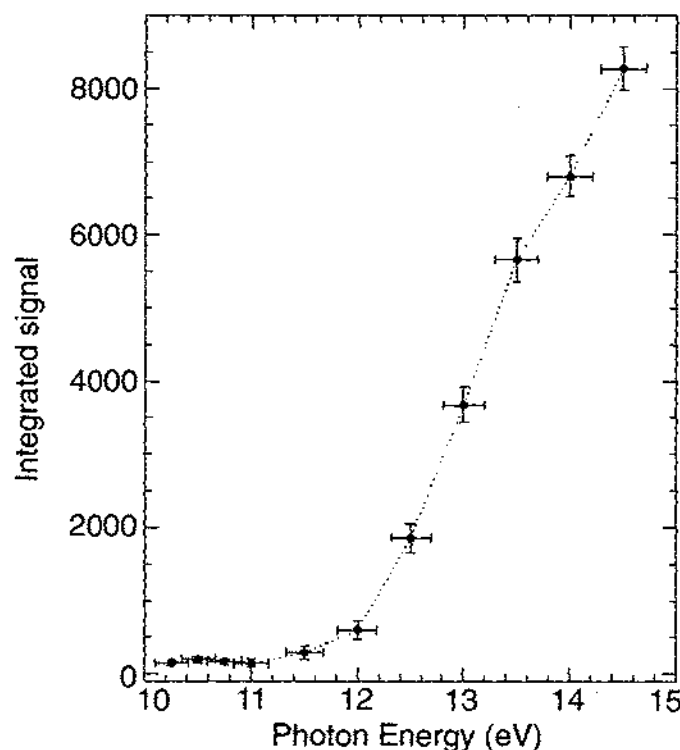


Figure 2. Photoionization-efficiency spectrum for ClCO from 193-nm dissociation of oxalyl chloride. [Figure courtesy of Arthur Suits, LBNL.]

2.2.2 New Molecules

Recent work has suggested the possible formation of energetic, metastable tetraoxygen species produced in the nonequilibrium combination of a pulsed discharge with a supersonic expansion. The use of tunable undulator radiation will allow for direct one-photon probing of this species to determine its energy and to aid in assigning its structure. These "physical synthesis" methods, similar to those that produced C_{60} , might conceivably produce other such novel molecules. The combination (described in Section 3) of a high-throughput monochromator system and the imaging end station will be well suited to the investigation and characterization of such species using simple photoionization-efficiency measurements or imaging photoelectron spectroscopy.

2.2.3 New Chemistry

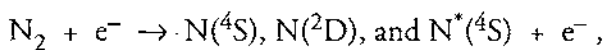
Molecular beams enable one to prepare highly reactive species under carefully controlled conditions, allowing one to study the elementary reactions that combine to yield the macroscopic chemistry taking place in the atmosphere, in an engine, or in interstellar space. Often these reactions will involve new chemistry with novel reactants or products. The recent crossed-beam study of the reaction of carbon atoms with acetylene is a case in point—the dynamics of these reactions and their importance to interstellar chemistry were unknown and the product C_3H isomers not well characterized. As detailed further in the section on astrochemistry below, tunable soft VUV ionization in End Station One will allow direct insight into this new chemistry because product isomers and electronic states may be identified directly and compared to *ab initio* calculations. Similar considerations apply to studies in combustion chemistry. As new molecular-beam sources of radicals or excited atoms are developed, new reactions will inevitably be revealed. This underscores the importance of parallel laboratory development of molecular-beam sources of radicals.

2.3 Atmospheric Chemistry and Global Change

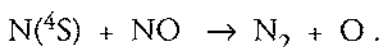
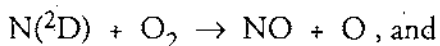
Substantial opportunities exist for increased understanding of the fundamental reactions involved in atmospheric chemistry and global change. The availability of soft x-ray radiation can be used to characterize aerosols, and the tunability in the ultraviolet can be used for selective ionization to determine branching ratios in key reactions. Since photoabsorption cross sections as a function of wavelength for such important classes of molecules as CFCs and HCFCs are not known, both the Working Groups on Atomic, Molecular, and Optical Physics and on Chemical Dynamics have recognized the important role the ALS has to play in atmospheric chemistry (see also Section 2.2.5 of the report of the Working Group on Atomic, Molecular, and Optical Physics).

2.3.1 Electron Scattering from N_2

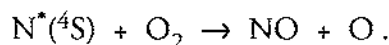
The NO budget in the upper atmosphere depends critically on the product state distribution resulting from dissociative electron scattering with N_2 . In the 10-eV to 20-eV range, we have



where N^* refers to translationally excited nitrogen atoms. These nitrogen atoms result in the production and depletion of NO via

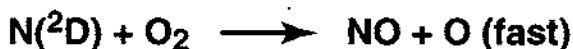
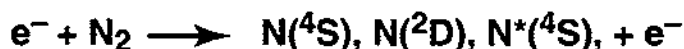


In addition, translationally hot $N^*(^4S)$ can form NO via



Calculations shown in Figure 3 demonstrate that the concentration of NO changes by over an order of magnitude if the branching ratio for production of $N(^2D)$ and $N^*(^4S)$ atoms changes by only a few percent from a ratio around 0.5. It would therefore be very useful to measure the branching ratio in the laboratory as a function of electron energy. This experiment can be performed by introducing a low-energy electron gun into either End Station One or the new proposed end station (see Section 3) and then using tunable VUV ionization to detect selectively the various electronic states of the atomic-nitrogen products.

Atmospheric chemistry: the NO budget



\therefore deviations from 50% $N(^4S)$, $N(^2D)$
have large effects on [NO]

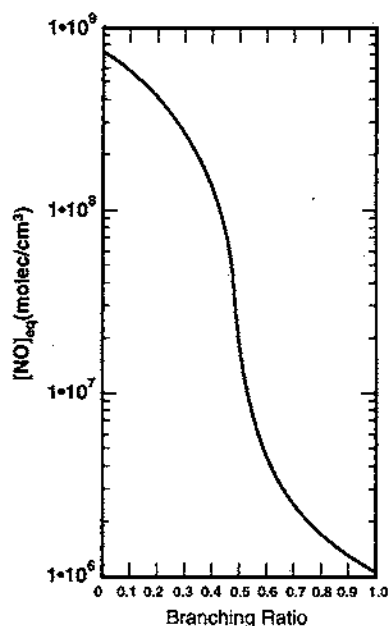
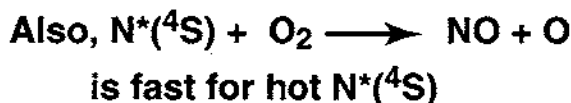


Figure 3. Calculations show that the concentration of stratospheric NO varies strongly with the branching ratio for production of $N(^2D)$ vs. $N^*(^4S)$ in the dissociative electron scattering from nitrogen. [Figure courtesy of S. Solomon, NOAA, University of Colorado.]

2.3.2 Aerosols

Combustion aerosols from crude-oil flaming, from Diesel motors or other industrial combustion, and from wood smoke from forest or savanna fires have the potential at some atmospheric altitudes to counteract the warming effects of anthropogenic gases (CO_2 , CFC, CH_4 , N_2O , O_3), while at other altitudes they pose a serious public-health threat. Submicron carbonaceous particles ($0.03 \mu m$) containing primarily organic and/or black carbon material can often combine with sulfur compounds, the major component of aerosols. These particles then cause cooling perturbations on the overall greenhouse warming and also influence regional anomalies of the climate. Understanding these particles is thus an important component of our ability to understand and predict climate change.

One pressing issue is to investigate the mixing of these particles with water droplets in clouds and to examine their reactivity with atmospheric gases under solar radiation. The photochemical reactions on the surface of such aerosols represent a new class of heterogeneous chemical reactions whose understanding is necessary for inclusion in atmospheric models. There are various types of aerosols to be considered: pure carbonaceous particles, pure water aerosols, hydrophilic carbonaceous particles, carbonaceous particles seeded with metal ions (such as iron) or inorganic material (Ca, SiO₂), etc. The oxidation of SO₂ by water to produce sulfates or the reactions involving NO_x-NO_y cycles are typical processes to be considered. According to current laboratory experiments investigating chemiluminescent reactions on very large rare-gas clusters (several thousands of atoms), the reaction rarely involves a one-to-one molecular interaction but rather the formation of dimers or trimers or even microclusters of reactants. It would be ideal to build an experiment incorporating a direct probe of such microclusters by in-situ x-ray absorption [near-edge x-ray absorption fine structure (NEXAFS, also known as XANES) or extended x-ray absorption fine structure (EXAFS)]. The tunability and the brightness of the ALS in the soft-ray and x-ray spectral regions would provide the chemical selectivity necessary to select the microclusters out of the other products in the small region of the reaction. The x-ray absorption spectrum would give directly the structural and chemical-bonding information that is impossible to obtain using normal laboratory instruments.

Novel types of experiments can also be envisaged based on carbonaceous, soot-like aerosols produced by infrared laser pyrolysis of hydrocarbons that are quite representative of a combustion process. Reactant gases might be incorporated onto the surface of these aerosols by the "pick-up" technique or by a crossed beam method. At the center of the reactor, a cw visible-UV laser can be switched on to trigger the photoreaction. Several probe techniques such as mass spectrometry and visible chemiluminescence can be used together with the synchrotron x-ray probe to complement the determination of the reaction mechanism.

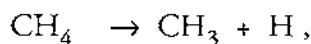
2.4 Astrochemistry

As a third-generation synchrotron source, the ALS offers many unique opportunities for advancement in understanding processes important in planetary atmospheres, in astrophysics, and even in the cosmology associated with the planet formation. The ALS can be used to study branching ratios for the production of different photochemical products as a function of the wavelength of the light (see Section 2.1.2). The unique capability stems from selective ionization based on the tunability of the undulator radiation.

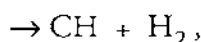
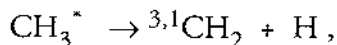
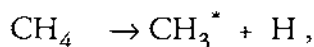
2.4.1 Photochemical Branching Ratios as a Function of Wavelength

Branching ratios for photodissociation and photoionization are important for understanding comets and planetary atmospheres. First, consider saturated hydrocarbons. These molecules are important in the atmospheres of the giant planets and their satellites, in comets, and in the interstellar medium. The most important wavelength for studying them is Lyman- α . Even with four-wave mixing and resonant sum or difference frequency mixing, it is difficult for laboratory lasers to obtain more than 10¹¹ photons per laser pulse at this wavelength. The low flux precludes determining branching ratios among possible dissociation channels of hydrocarbons. Although the dissociation of methane has recently been reinvestigated by detecting the hydrogen atoms with laser-induced fluorescence (LIF) and by imaging, these studies did not adequately distinguish between the four processes of

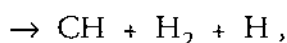
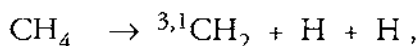
(1) simple C-H bond fission leading to stable CH_3 radicals,



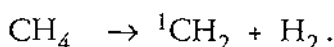
(2) sequential dissociation into three fragments,



(3) simultaneous dissociation into three fragments,



or (4) molecular elimination,



The ability to determine the velocity of the heavy fragment would certainly aid in sorting out these possibilities. The imaging apparatus at the ALS could use the first harmonic to dissociate the CH_4 and the second harmonic to detect the heavy fragments. Similar problems occur for the photolysis of other saturated hydrocarbons, such as ethane and propane, and for alkynes, such as acetylene.

2.4.2 Reaction Dynamics

Recent work by Arthur Suits and Yuan Lee at LBNL and the University of California, Berkeley, using the crossed-molecular-beam technique has shown the importance of neutral reactions in the synthesis of carbon-bearing molecules in interstellar space. These studies were hampered by the inability to identify the radical product isomers directly. The crossed-beam method is ideal for detailed study of these reactions involving highly reactive radicals and atoms, since products are detected before subsequent chemistry takes place obscuring the processes of interest. End station one, with the tunable VUV probe, will aid greatly in identifying the primary products of these reactions, helping to unravel the complex chemistry in interstellar clouds and planetary atmospheres.

2.5 Cluster Dynamics and Spectroscopy

The high photon flux of the ALS allows coincidence measurements that can greatly improve our understanding of the spectroscopy and dynamics of clusters, clearly an exciting area of opportunity for chemical dynamics and AMO physics in the VUV (see also Section 2.1 of the report of the Working Group on Atomic, Molecular, and Optical Physics).

2.5.1 Photoionization/Photoelectron Coincidence Spectroscopy of Clusters

Photoelectron spectroscopy of size-selected clusters reveals how electronic and vibrational structure evolves from the molecular to the macroscopic, therefore bridging the gap between small-molecule chemical physics and materials science. Numerous experiments of this type have been performed on negative cluster ions of carbon, silicon, germanium, and mixed species, such as gallium arsenide and indium phosphide. However, analogous studies of neutral clusters have been far more difficult to perform because such clusters cannot be mass-selected prior to spectroscopic interrogation. To deal with this issue, we propose to perform photoelectron-photoion coincidence studies on these clusters at the ALS. Clusters will be generated in a laser ablation/molecular beam source using a high repeti-

tion rate (about 1 kHz) laser. The experiments can best be carried out on the proposed chemical-dynamics imaging end station with the high-throughput medium-resolution monochromator (see Section 3), since 10-meV resolution is about what one needs.

2.5.2 Inner Electron Spectroscopy and Photodissociation of Ion Clusters

Studies of ion clusters are appealing because they are readily size-selected, so that there is no ambiguity concerning their mass. However, since ion clusters are typically produced in much lower quantities than neutral species, all spectroscopy experiments performed to date have been restricted to the visible and near ultraviolet, where powerful lasers are available. The high photon flux and low emittance of the ALS will allow us to extend these studies to the vacuum ultraviolet region and beyond. The VUV spectroscopy of ion clusters offers a novel probe of their electronic structure. Specifically, one can map out the evolution of the more tightly bound orbitals and compare their energies to those of the highest occupied molecular orbitals (HOMOs) probed in the visible/near UV. This measurement can be done for clusters ranging from rare-gas cluster ions to carbon and semiconductor ions. Experimentally, the most feasible means of performing these experiments is to detect photodissociation products. One can collinearly overlap a mass-selected cluster-ion beam with the beam from the ALS, and use a secondary-mass spectrometer to analyze and detect product-ion fragments.

2.5.3 Helium/Argon Droplets

Another experiment along these lines involves generating a beam of very large, cold helium clusters (10,000 to 100,000 atoms) and passing it through a graphite oven; the result will be exceedingly cold carbon clusters adsorbed onto (or absorbed into) a much larger helium cluster. Studies to date in France and in the U.S. have typically used detection of laser-induced fluorescence or chemiluminescence to probe the dynamics in these systems, but clear opportunities exist for applications of synchrotron radiation to probe the products directly using photoionization, photoelectron spectroscopy, or fluorescence methods. One could then measure the ionization potentials, photoelectron spectra, and ion-fragmentation spectra for these clusters. An intriguing possibility is to probe these species with much higher photon energies (about 1 keV) to perform EXAFS and other x-ray based spectroscopies; the resulting structural information would complement more common experiments in the visible and ultraviolet.

2.6 Plasma Chemistry

Studies of plasma chemistry are relevant to the semiconductor industry, planetary atmospheres, and material research. The modeling of plasma processes requires accurate absolute total cross sections or rate constants of ion-molecule and ion-radical reactions in the kinetic energy range from thermal to about 100 eV. Because these quantities are also of fundamental interest, this area of research is also important to the atomic, molecular, and optical physics community (see Section 2.1 of the report of the Working Group on Atomic, Molecular, and Optical Physics). Since the temperature varies greatly in different plasmas, it is necessary to measure absolute cross sections of internally excited atomic and molecular ions over a wide range of collisional and vibrational energies. The high sensitivity in photoionization achieved using the photoion-photoelectron apparatus at the ALS would allow the reactivity studies of ions in very high vibrational states. Owing to the very high photoelectron-energy selectivity demonstrated in PFI-ZEKE measurements, the further development of the photoion-photoelectron apparatus associated with the Chemical Dynamics Beamline will offer unique capa-

bilities for studies of mode- or state-selected ion-molecule reaction dynamics. Specifically, the reaction cross sections involving diatomic and simple polyatomic hydride cations should be measurable at the rotationally state-selected level.

Cross-section measurements for ion-radical reactions are an unexplored field. Owing to the high VUV flux of ALS undulator radiation (10^{16} photons/sec at 2.2% bandwidth), the preparation of state-selected neutral atoms and radicals for reactive studies should be possible. Atoms and radicals in specific internal states can be prepared by photodissociation of appropriate precursor molecules. Knowing the photodissociation cross sections would allow the reliable determination of the number density for the photoproduct thus prepared.

2.6.1 Photodissociation of State- or Energy-Selected Molecular Ions

Spectroscopic and thermochemical information about gaseous ions may be obtained using laser-photodissociation spectroscopy, which involves the monitoring of daughter ions as a function of the energy of the laser radiation. Earlier experiments used electron-impact ionization for ion preparation, and the ions thus formed were thermally excited over a distribution of rotational and vibrational states. The thermal excitation of the precursor ions makes the analysis of the photodissociation spectrum difficult. In addition, hot-band excitations also shift the dissociation threshold to a lower energy.

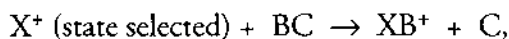
These problems can be overcome by use of molecular photoionization and molecular beams. Photoionization favors processes with a small change in rotational quantum number, so that molecular ions in the ground vibrational state can be efficiently prepared with negligible rotational excitation in a free jet by photoionization at photon energies near the ionization threshold. State-selected or energy-selected molecular ions can be prepared by photoelectron-photoion coincidence (PEPICO) techniques for photodissociation studies. Baer and coworkers have applied the PEPICO technique to energy-select ions and subsequently photodissociate them with a pulsed excimer laser. The kinetic-energy-release distributions derived for the product ions provide information about the dynamics of unimolecular dissociation. We plan to develop this technique for routine studies of the photodissociation dynamics of vibrational- and electronic- state-selected diatomic and triatomic ions.

2.6.2 Dynamics of State-Selected Ion-Molecule Reactions

The U10 undulator, in connection with a high-resolution monochromator, is particularly useful for experiments requiring highly monochromatic radiation of high intensity and makes it feasible to perform chemical-dynamics experiments that were previously impossible. As described above, the system is particularly well suited for preparing ions in well-defined states. One area of future investigation is to explore state- or energy-selected ion reactions.

Studies of the chemistry of state- or energy-selected ions are important for the fundamental understanding of ionic processes relevant to organic, inorganic, atmospheric, interstellar, plasma, and materials chemistry. Many ion-molecule reactions relevant to the Earth's ionosphere involve electronically excited atomic oxygen and nitrogen ions. Because of the difficulties in preparing these ions, reliable cross sections for many important atmospheric ion-molecule reactions have not been examined in detail. We plan to develop a PEPICO apparatus for ion-molecule reactions that incorporates mass-spectrometric and rf-octopole ion-guide techniques in order to measure for state-selected cross sections of ion-molecule reactions of planetary interest.

The aim is to investigate ion-molecule and ion-cluster dynamics by using ions in electronically well-defined states. Reactions are of the type



where X is a rare gas (He, Ne, Ar, Kr, Xe) and BC is a diatomic or polyatomic molecule (e.g., CO, CO₂, CH₄, etc.). A particular state is selected by using an ion-electron coincidence technique, which distinguishes between different electronic states. This method can also be applied to produce molecular ions in a particular vibronic state to use as reagent ions in ion-molecule reactions. An example is shown in Figure 4, which demonstrates that bending levels of OCS⁺ can be selected by the PEPICO technique. The investigation of reactions between state-selected ions and clusters will also be considered in order to study energy- and charge-transfer processes in such systems.

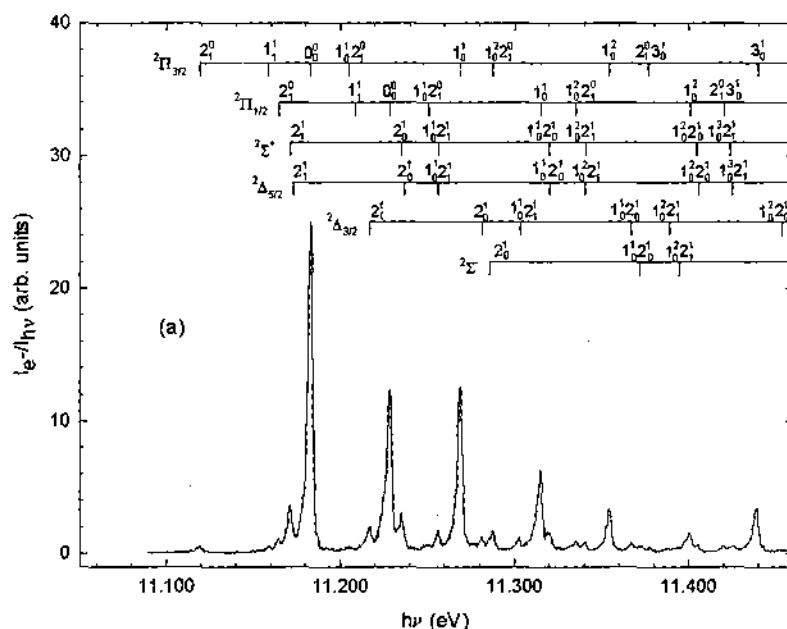


Figure 4. This spectrum showing a fully resolved vibrational structure for OCS⁺ demonstrates that the PEPICO technique can select the bending levels of OCS⁺ for mode-selective dynamics studies. [Figure courtesy of C. Ng, Iowa State University.]

2.7 Chemistry in Real Time

The beginnings of chemical kinetics involved the mixing of reactants and the observation of the time dependence of changes in the system. From this beginning there has been a continuing quest to improve the time resolution of the experiments to enable the detailed observation of the motions of the molecular reactants on the time scale of the motion of the individual atoms. These ultrafast time-dependent studies began with flash photolysis 50 years ago with a resolution of microseconds and were subsequently twice revolutionized, first by the development of lasers and second by mode locking. The recent development of Ti:sapphire chirped pulse lasers has caused yet another revolution, placing this technology in the hands of scientists that are not full-time laser developers.

We now have the opportunity to observe chemical-reaction processes in real time, watching hydrocarbon bonds in a single excited molecule break simultaneously or sequentially—and understanding why it happened that way! We can begin to choose the domain (time or frequency) that provides the

optimum density of information. The future lies in understanding and predicting the behavior of systems of greatly increased complexity (large molecules, clusters, solvated reactants, molecules at interfaces) where the number of degrees of freedom is too numerous to allow accurate computation and high-resolution frequency-domain data may not be amenable to analysis. Most needed are ultrafast techniques that enable one to investigate selectively only those degrees of freedom that are important to the chemical process. The most obvious such information concerns the positions of the nuclei and the electronic state of the reacting partners. In solution, solids, or clusters, we must know the positions of the neighbor atoms and molecules. It would appear that inner-shell excitation and level shifts may be a particularly effective probe to provide this time-dependent structural information. This will require the development of intense, tunable, ultrafast light pulses in the ultraviolet/near x-ray region. The third- and fourth- generation light sources may have a truly unique role to play in this endeavor.

2.8 Photoionization Dynamics of Complex Molecules

Photoionization is becoming increasingly important as a probe of chemical systems, be they complex molecules, transition states, clusters, or radicals. What is not as obvious is that the photoionization dynamics for molecular systems provides a useful means of developing a deeper understanding of molecular scattering. For both of these reasons, the ALS will be a useful tool for developing a clear understanding of how electrons are ejected from molecular systems and, in so doing, how electronic and nuclear degrees of freedom are coupled in fundamental and theoretically tractable systems. It should be noted that a fundamental understanding of electron-ejection dynamics for simple systems has already led to important applications; for example, the field of NEXAFS spectroscopy of adsorbates on surfaces. It is very likely that an understanding of photoejection dynamics can lead to analogous applications to more complex materials and biological systems. A clear understanding of photoelectron dynamics for complex systems, such as polyenes and heterocyclic ring structures, can be of fundamental interest in chemical and molecular physics.

There are at least two possible experiments that one can envision, although it is likely that many others will emerge. First, it would be of great interest to obtain vibrationally resolved photoelectron spectra on polyatomic systems over a broad energy range for both valence- and core-electron ejection in order to study how the ionization process responds to changes in molecular geometry. Second, it would be informative to study how the ionization dynamics behave far from threshold for molecular clusters. Both of these experiments have the potential of understanding how electrons become quasibound in real systems, and such information is not accessible via other means. The high resolution of the ALS beam on end-station two should make interesting studies possible on such complex systems.

Related studies on dissociative ionization processes and the decay dynamics of superexcited states promise insights into the nature of the coupling among the electronic states at these energies above the first ionization potential, as well as providing valuable data for thermochemical cycles. The imaging apparatus and high-throughput monochromator system mentioned above will enable coincidence measurements of the complete energy and angular distributions for these processes, thereby providing unprecedented insight into the lifetimes, decay pathways, product branching, and coupling mechanisms in these systems.

3. Future Capabilities

The ALS represents the world's most intense source of continuously tunable VUV light in the 5-eV to 30-eV region. This high intensity has been exploited in two branch lines on Beamline 9.0.2, one of which incorporates a 6.65-m Eagle monochromator to perform very high-resolution studies of photoionization dynamics and threshold photoelectron spectroscopy, while the other relies on the broadband "white beam" of the undulator with its inherent 2.2% energy bandwidth to perform selective soft ionization of reaction products. An important innovation for chemical-dynamics studies at the ALS is to take advantage of the new velocity-map imaging technique in conjunction with a high-throughput monochromator system. This combination will considerably expand the experimental opportunities and broaden the appeal of studies on the beamline to a larger community in the field of chemical dynamics. New experimental opportunities include spectroscopy and photodissociation dynamics of radicals (Section 2.1), cluster dynamics and spectroscopy (Section 2.5), identification and characterization of novel metastable molecules and superexcited states and their decay mechanisms (Section 2.2), and new approaches to the study of photoionization dynamics in complex systems (Section 2.8).

A moderate-resolution, high-throughput monochromator system has been designed for application on the beamline in conjunction with an end station based on ion imaging. The monochromator, whose performance is summarized in Table 1 along with the characteristics of the existing branchlines, has a high-efficiency, moderate-resolution 3-m Eagle design. The new end station incorporates dual imaging detectors for recording energy and angular distributions of electrons and ions, singly or in coincidence. This combination, joining many of the strengths of the two existing end stations with the powerful imaging technique, promises greatly enhanced experimental versatility. This versatility comes from the inherent multiplexing nature of the imaging technique and the high flux of the monochromator.

Table 1. Characteristics of Chemical Dynamics Branch Lines

Branch Line	1	2	3 (proposed)
Source	"White Beam"	6.65-m Eagle	3-m Eagle
Resolution, $E/\Delta E$	35 to 50	3000 to 75,000	50 to 1000
Flux	10^{16}	10^{12}	10^{14}
(at resolution)	50	3000	1000

4. Summary

The Chemical Dynamics Beamline at the ALS along with its dedicated end stations has already begun to make a substantial impact of in the area of combustion. As the user base grows and as the new opportunities in atmospheric chemistry, cluster chemistry, plasmas, and astrochemistry augment further advances in combustion, many more of the unique features of the beamline will be exploited to extend the depth and range of chemical dynamics. The high likelihood of major advances and the importance of the problems being addressed argue strongly for increased support of the Chemical Dynamics Beamline.

Appendix A

The ALS as a Source of Intermediate-Energy X Rays

Howard Padmore, Advanced Light Source

1. Introduction

The Advanced Light Source (ALS) was optimized to produce extremely high flux and brightness in the vacuum-ultraviolet (VUV) and soft x-ray regions using undulator sources. It is also, however, an excellent source of intermediate-energy x rays, from 1 keV to 15 keV, and here the properties of various ALS sources, existing and proposed, are benchmarked against the performance of the Advanced Photon Source (APS), National Synchrotron Light Source (NSLS), and Stanford Synchrotron Radiation Center (SSRL). Although the core program of the ALS will always be in the lower energy region, the complementarity of higher energy techniques and the potential to have a large capacity in this spectral range are powerful arguments for the full exploitation of the capability of the ALS in the intermediate-energy x-ray region.

The flux and brightness are widely used to characterize the quality of a light source and are presented here for the ALS in comparison to other DOE light sources. In the case of microfocus experiments, in general the figure of merit is brightness. For experiments in which neither good angular collimation nor a small focus size are required, flux is the figure of merit. Several classes of experiment, however, have a figure of merit that is somewhere between flux and brightness, and to evaluate the quality of the source, the flux lying within the position-angle or phase-space acceptance of the experiment has to be evaluated. For example, vertical brightness is required in experiments that involve grazing-incidence reflection or diffraction. The demand for brightness is due to the small apparent sample size at small angles of incidence and the required high degree of angular collimation. Another example, in which the figure of merit is closely related to the horizontal brightness, is diffraction from protein crystals where crystal sizes are often a few hundred microns and typical angular collimation is a few milliradians. Care therefore has to be exercised in directly using flux and brightness to compare the characteristics of light sources.

In this note the ALS performance is benchmarked against existing light sources and against an upgraded machine at SSRL. Finally the performance of the ALS with incremental improvements is compared to the APS.

2. Existing Sources

In this section, the performance of the ALS at its standard operating energy of 1.9 GeV is benchmarked against the existing APS, NSLS, and SSRL machines. The graphics indicate for the most part the types of radiation source, so comments are given here only about specific devices and where clarification is needed. The accelerator parameters are given in Table 1 and the radiation-source parameters in Table 2. Note that the accelerator parameters are not fixed in time for any machine, and incremental improvements are constantly being made to increase brightness, for example by a reduction of the vertical emittance. In Figures 1 and 2, the flux and brightness of ALS bend-magnet and wiggler sources are compared to those of the APS bend-magnet, undulator A, and wiggler sources. Figures 3 and 4 show the flux and brightness comparison for selected NSLS sources—a bend magnet, in-vacuum undulator (IVUN), a permanent-magnet wiggler, and a superconducting wiggler. Figures 5 and 6 show the same comparison for SSRL radiation sources—a bend magnet and 15-, 26-, 30- and 54-pole wigglers. In summary, it can be concluded that in terms of flux, the APS wiggler is the highest output device, with the ALS wiggler being competitive with all the others examined to at least 15 keV. The APS undulators offer extraordinary brightness at high energy, with an advantage over the ALS wiggler of around 300 at 10 keV. The ALS and NSLS wigglers have a similar performance and have more than an order of magnitude advantage over the brightest SSRL wiggler at 10 keV. A surprising result is that an ALS bend magnet has a higher brightness than the SSRL 54-pole wiggler up to 9.5 keV and higher than the 15-pole wiggler up to 14 keV.

Table 1. Accelerator parameters.

Source	E (GeV)	I (mA)	ϵ_h (m·rad)	ϵ_v (m·rad)	β_h (ID, m)	β_v (ID, m)	D_x (ID)	β_h (bend, m)	β_v (bend, m)	D_x (bend)	$\delta E/E$
ALS	1.9	400	6×10^{-9}	6×10^{-11}	11.2	4.2	0	0.85	1.46	0.094	8×10^{-4}
APS	7.0	100	5.7×10^{-9}	1.3×10^{-10}	14.2	10.1	0	1.8	18.4	0.085	1×10^{-3}
NSLS	2.58	500	9.4×10^{-8}	1×10^{-10}	1.1	0.41	0.15	1.6	10.5	0.34	8×10^{-4}
SSRL	3.0	100	1.3×10^{-7}	1.3×10^{-9}	16.5	1.9	1.05	2.8	24	0.56	7×10^{-4}
SPEAR3	3.0	200	1.8×10^{-8}	1.8×10^{-10}	14.5	7.0	0	1.0	7.0	0.1	9×10^{-4}

Table 2. Radiation Sources.

Source	Bend Field (T)	Undulator	Wiggler	Wiggler	Wiggler	Wiggler
ALS	1.27 & 5.0	$\lambda_0=23\text{mm}$ N=40	$\lambda_0=160\text{ mm}$ N=37 $B_0=2.1\text{ T}$			
APS	0.6	$\lambda_0=33\text{mm}$ N=70	$\lambda_0=85\text{ mm}$ N=56 $B_0=1.0\text{ T}$			
NSLS	1.22	$\lambda_0=11\text{mm}$ N=31	$\lambda_0=120\text{ mm}$ N=27 $B_0=1.0\text{ T}$	$\lambda_0=174\text{ mm}$ N=5 $B_0=5\text{ T}$		
SSRL	0.77		$\lambda_0=260\text{ mm}$ N=15 $B_0=1.9\text{ T}$	$\lambda_0=175\text{ mm}$ N=26 $B_0=2.0\text{ T}$	$\lambda_0=129\text{ mm}$ N=30 $B_0=1.5\text{ T}$	$\lambda_0=70\text{ mm}$ N=54 $B_0=1.0\text{ T}$
SPEAR3	1.19	$\lambda_0=33\text{mm}$ N=70	$\lambda_0=260\text{ mm}$ N=15 $B_0=1.9\text{ T}$	$\lambda_0=175\text{ mm}$ N=26 $B_0=2.0\text{ T}$	$\lambda_0=129\text{ mm}$ N=30 $B_0=1.5\text{ T}$	$\lambda_0=70\text{ mm}$ N=54 $B_0=1.0\text{ T}$

λ_0 is the undulator period, N is the number of poles, and B_0 is the peak field.

3. Comparison to the Spear3 Upgrade of SSRL

The comparison of the ALS to an upgraded SSRL with the SPEAR3 lattice is shown in Figures 7 and 8 for flux and brightness, respectively. In terms of flux, the wiggler performances are similar, and the SPEAR3 bend magnet now has a significantly better performance than the ALS for most of the energy range with an advantage of 4 at 10 keV. In terms of brightness, the ALS wiggler and SPEAR3 54-pole wiggler have similar performance over the whole energy range, and the bend magnets become equivalent at 12.5 keV, with the ALS having better performance at lower energy.

Storage rings and radiation sources can be incrementally improved over time, offering significant performance advantages. Figure 9 and 10 show the flux and brightness of the ALS and the SPEAR3 machine with additional radiation sources. These are by no means a complete set, and clearly with advancing undulator and wiggler technology, as shown by the in-vacuum undulator pioneered at NSLS, substantial improvements can be made.

A 23-mm-period, small-gap undulator has been studied at the ALS to cover the important 1-keV to 4 keV energy range. The performance of this device in flux and brightness is similar to that of the APS undulator A proposed for SPEAR3, although the ALS device would have to use the first through fifth harmonics, whereas the higher energy of SPEAR allows a longer period and requires

only the first and third harmonics. The ALS device will tune down to around 300 eV. The use of small gaps also allows the development of more-optimum wigglers, and we have shown here a 50-mm-period device with a 5-mm gap and 40 poles. This device would be operated with two sets of additional quadrupoles to decrease the vertical and horizontal beta values to 0.5 m and 3 m, respectively. This, together with the reduction in length and peak oscillation amplitude, gives an increase in brightness of around a factor of eight at 10 keV.

A project was started in 1993 to investigate the possibility of replacing three of the 36 bend magnets in the ALS lattice with high-field magnets. This study matured into a construction project to build a prototype magnet, and after three years of research and development, the LBNL superconducting-magnet group recently produced a full-scale prototype that has routinely demonstrated a peak field of 6.5 T and a field at the source points of 5 T. This is now a mature technology; moreover, it requires only relatively minor changes to the machine and would have minimal impact on the emittance. Each bend magnet will give light into two ports, and each of these can be split into two beamlines. Three magnets therefore give us the potential to have 12 superconducting bend-magnet beamlines. As shown in Figures 9 and 10, these devices will have excellent performance to above 20 keV.

4. Comparison of Future ALS Sources to the APS

Finally, it is useful to benchmark the subset of possible future devices that we can add to the ALS to those available now at the APS. This comparison is shown in Figures 11 and 12. The 23-mm-period ALS undulator fills in the energy range below that covered by APS undulator A; the small-gap wiggler is competitive with the APS wiggler in terms of brightness; and the superconducting bend magnet offers very similar performance to an APS bend to above 20 keV. For those experiments requiring extremely high brightness in the x-ray range, for example phase-contrast microscopy and coherent scattering, the APS undulators offer outstanding performance. However, for a significant subset of experiments, the brightness of ALS devices may well be sufficient. The prospect of superconducting bend magnets seems to offer an outstanding opportunity in that it will give us a significant number of excellent high-energy x-ray sources for a low cost to complement the already excellent performance of our soft x-ray and VUV sources.

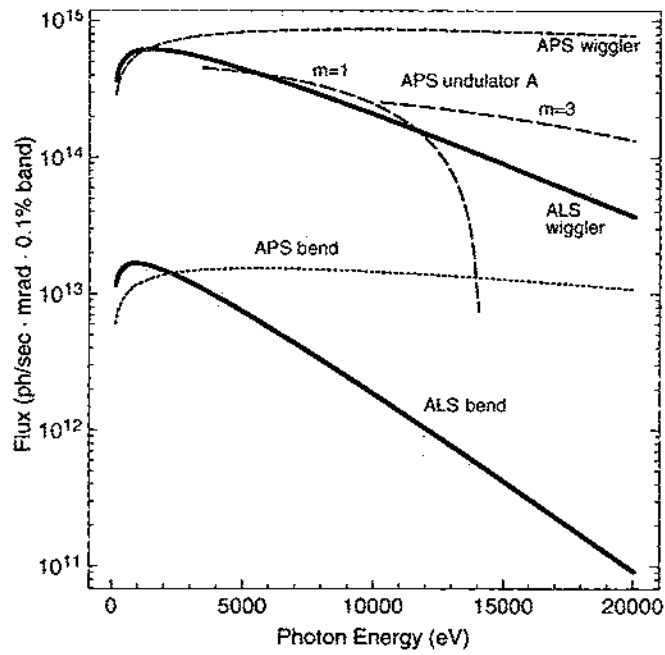


Figure 1. Flux of ALS and APS sources.

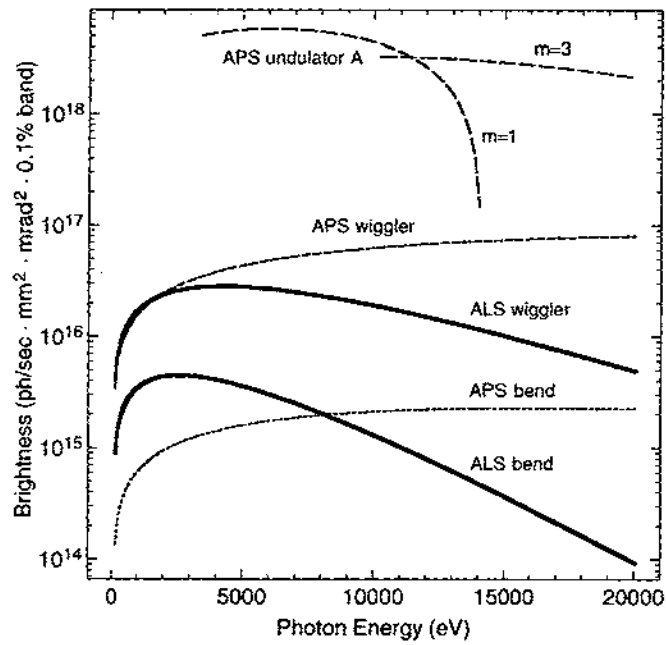


Figure 2. Brightness of ALS and APS sources.

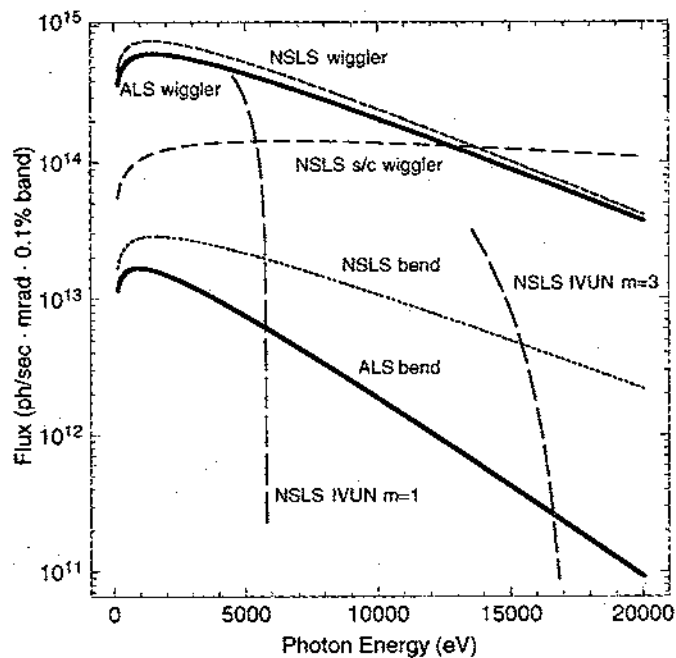


Figure 3. Flux of ALS and NSLS sources.

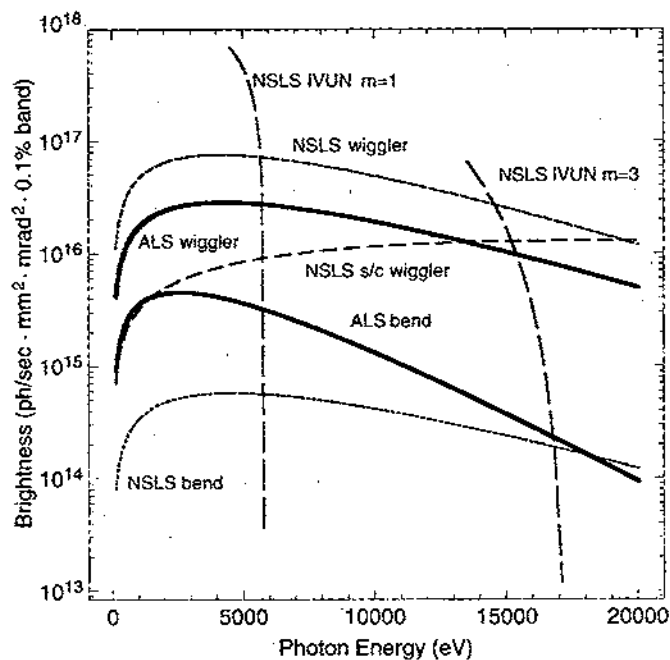


Figure 4. Brightness of ALS and NSLS sources.

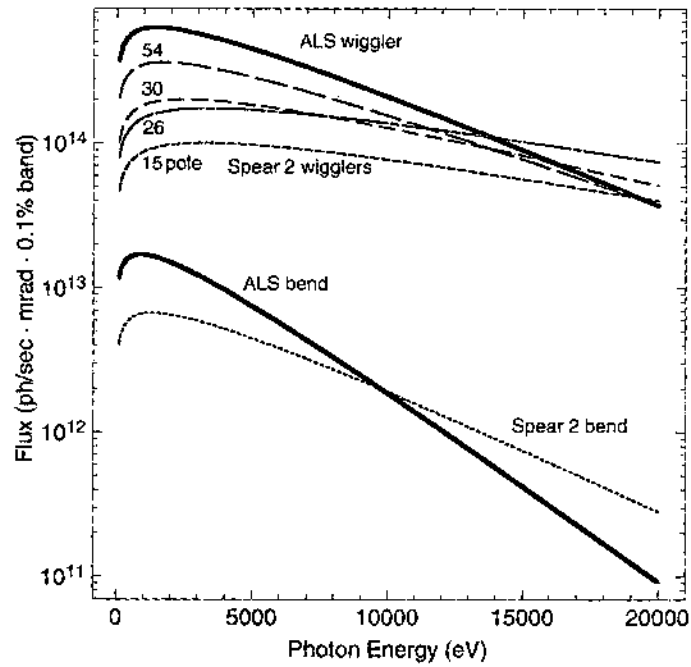


Figure 5. Flux of ALS and SSRL sources.

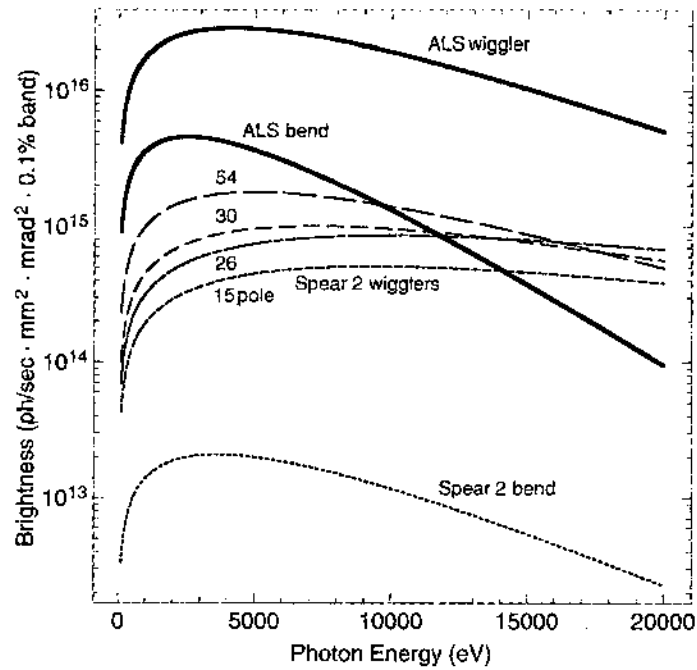


Figure 6. Brightness of ALS and SSRL sources.

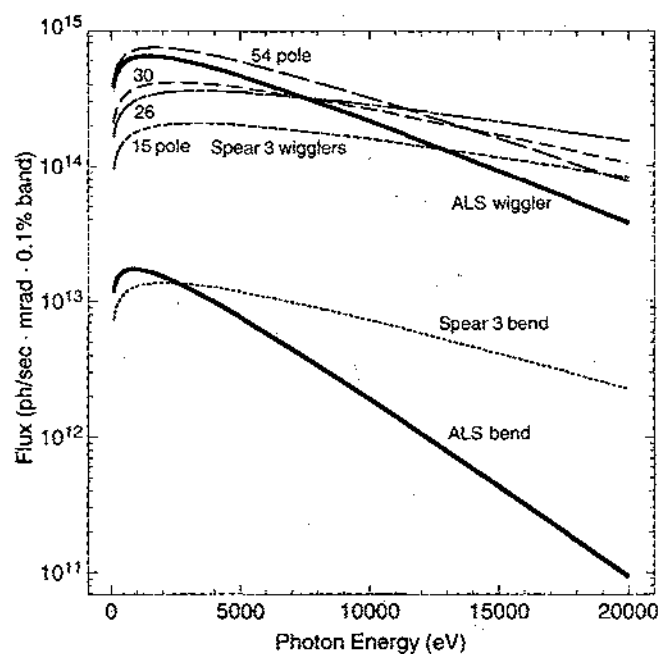


Figure 7. Flux of ALS and SPEAR3 sources.

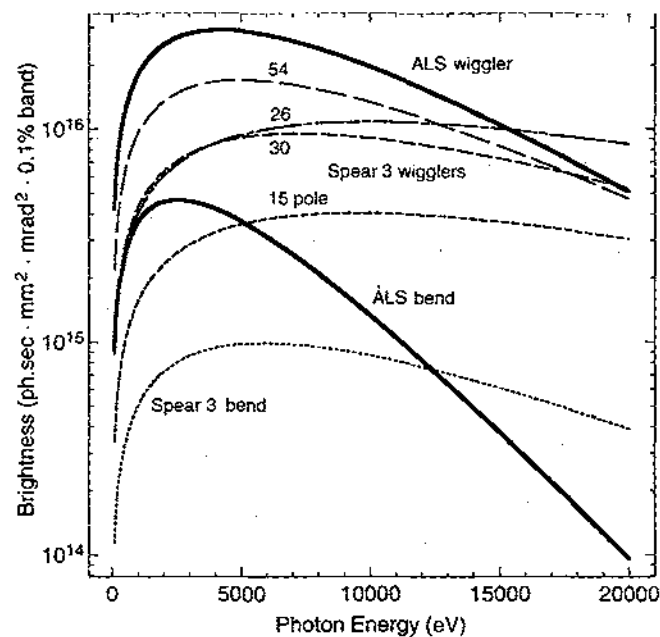


Figure 8. Brightness of ALS and SPEAR3 sources.

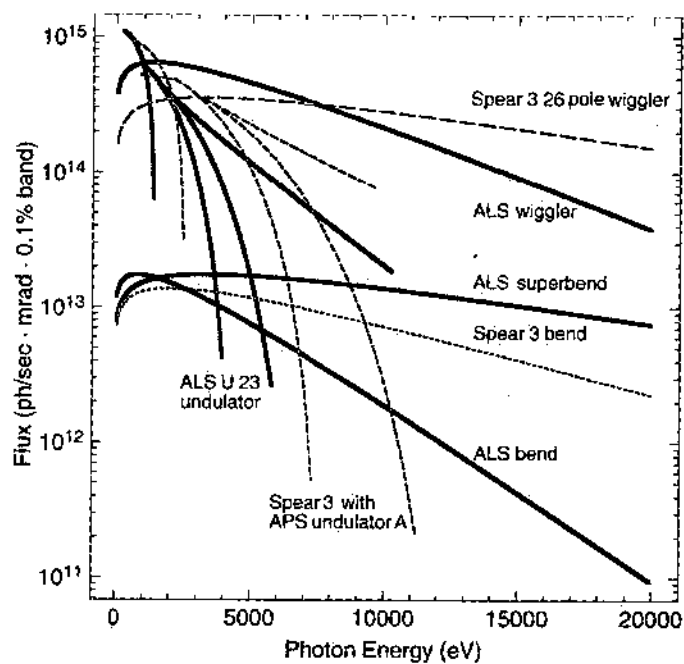


Figure 9. Flux of ALS and SPEAR3 with additional sources.

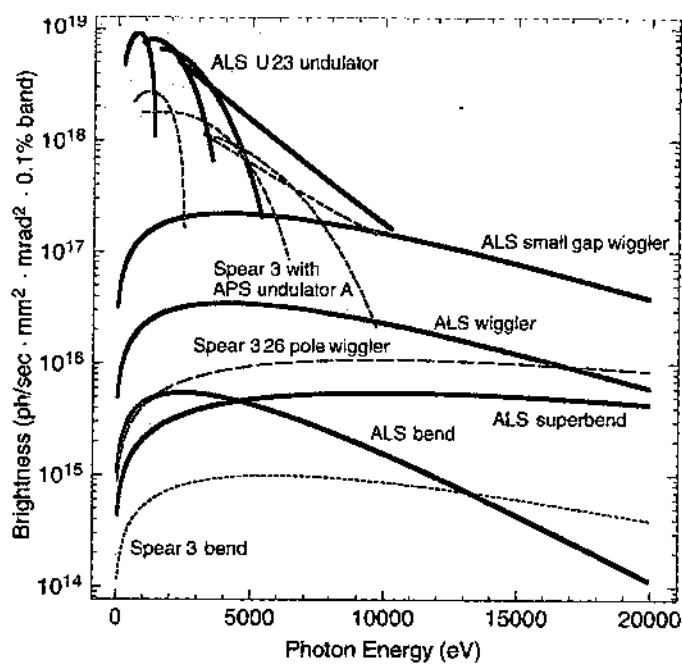


Figure 10. Brightness of ALS and SPEAR3 with additional sources.

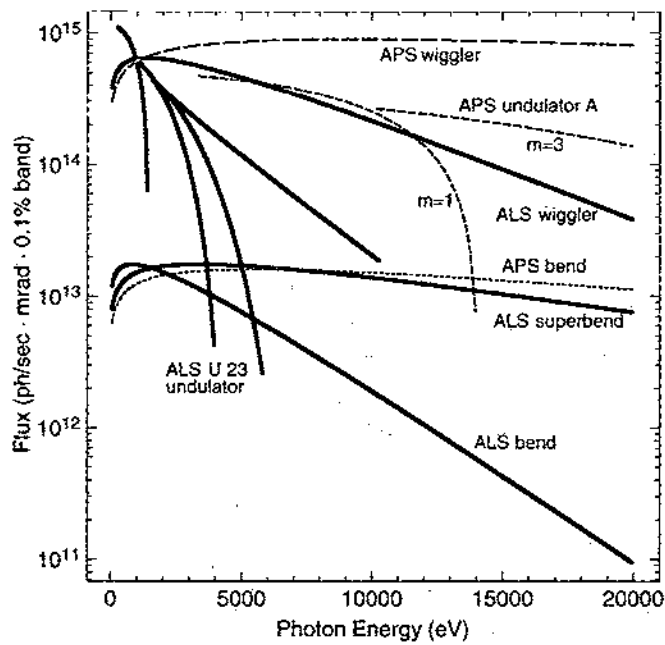


Figure 11. Flux of the ALS with superbends, a small gap undulator and a small gap wiggler and of the APS.

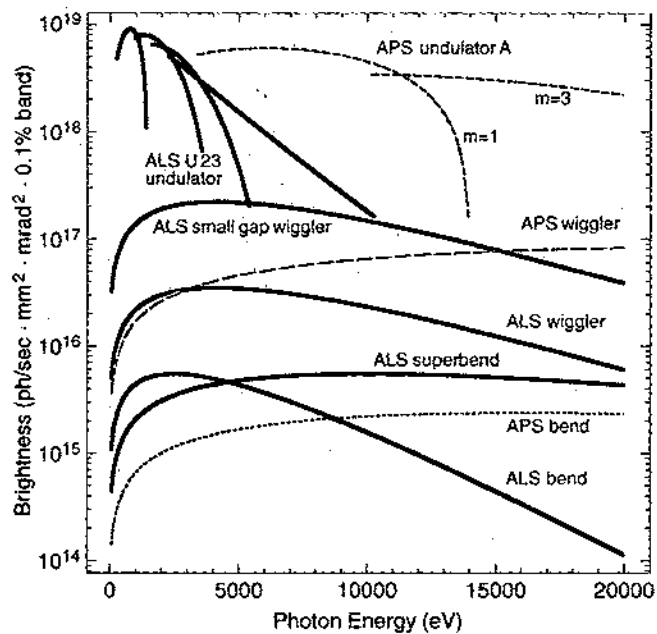


Figure 12. Brightness of the ALS with superbends, a small gap undulator and a small gap wiggler and of the APS.

Appendix B

Workshop Program

Scientific Directions at the Advanced Light Source

March 23—25, 1998

Program Agenda

Sponsors

Department of Energy, Office of Basic Energy Sciences
Ernest Orlando Lawrence Berkeley National Laboratory, Advanced Light Source
University of California, Office of the President

Chair

Yves Petroff, Director-General, European Synchrotron Radiation Facility

Charge

The goal of this workshop is to identify the elements of the most compelling scientific program for the ALS and to make recommendations for a roadmap to implement that program.

MONDAY, March 23

- 7:30 Registration
Ernest Orlando Lawrence Berkeley National Laboratory Bldg. 50 Auditorium
- 7:45 Bus Service from the Shattuck Hotel
- 8:00 Bus Service from the Durant Hotel
- 8:30—12:30 Plenary Session, Bldg. 50 Auditorium — Chair: Yves Petroff
 - 8:30 Welcome on Behalf of Berkeley Lab — Charles Shank
 - 8:55 Welcome on Behalf of BES — Patricia Dehmer
 - 9:20 Experience at a Third-Generation Source — Yves Petroff
 - 10:00 View from the European Commission Round Table — Giorgio Margaritondo
 - 10:15 Break
 - 10:40 Broken Electrons Forming Pairs? — A Photoelectron's Story of High- T_c Superconductivity — Zhi-xun Shen
 - 11:20 Role of the ALS in Addressing Microelectronics Technology Challenges — John Carruthers
 - 12:00 Organization of the Workshop — Neville Smith
 - 12:15 User Issues — Werner Meyer-Ilse
 - 12:30 Lunch
- 2:00 Working Group Sessions (presentations & discussions) until 5:30
- 6:30 Dinner @ Le Cheval, 1007 Clay St., Oakland

TUESDAY, March 24

- 8:30 Working Group Sessions (discussions & recommendations)
- 12:30 Lunch
- 1:00 Short Plenary Session (progress reports) Bldg. 50 Auditorium
- 2:00 Working Group Sessions (report writing)

WEDNESDAY, March 25

- 8:30 Plenary Session (feedback from Working Groups), Bldg. 50 Auditorium
- 12:00 Working Lunch/User Forum — Werner Meyer-Ilse, Pier Oddone
- 2:00 Adjourn

Working Groups

(1) Complex Materials

Chair: Ward Plummer, University of Tennessee

Facilitator: Zhi-xun Shen, Stanford University

Technical Advisors: Zahid Hussain, Scott Kellar, and Erik Gullikson, Lawrence Berkeley National Laboratory

Technical Writer: Art Robinson, Lawrence Berkeley National Laboratory

Working-group members: Massimo Altarelli, European Synchrotron Radiation Facility (France); Thomas Callcott, University of Tennessee Knoxville; C.T. Chen, Synchrotron Radiation Research Center (Taiwan); Jun-Liang Chen, Synchrotron Radiation Research Center (Taiwan); Jonathan Denlinger, University of Michigan; Makoto Doi, Lawrence Berkeley National Laboratory; Wolfgang Eberhardt, Forschungszentrum Jülich; David Ederer, Tulane University; Kwang Yong Eun, Korea Institute of Science & Technology; Atsushi Fujimori, University of Tokyo, Japan; Eric Gullikson, Lawrence Berkeley National Laboratory; Michael Hochstrasser, Pennsylvania State University; Craig Horne, Lawrence Berkeley National Laboratory; Zahid Hussain, Lawrence Berkeley National Laboratory; Scott Kellar, Lawrence Berkeley National Laboratory; Miles Klein, University of Illinois Urbana-Campaign; Guy Lelay, CNRS Université de Provence (France); Hong-Ji Lin, Synchrotron Radiation Research Center (Taiwan); Ingolf Lindau, Stanford Synchrotron Radiation Laboratory; Martin Magnuson, Uppsala University (Sweden); Giorgio Margaritondo, IPA-EPFL (Lausanne, Switzerland); Nils Mårtensson, University of Lund (Sweden); Maurizio Matteucci, National Research Council (Italy); Joseph Nordgren, Uppsala University (Sweden); Se-Jung Oh, Pohang Light Source (Korea); Joe Orenstein, University of California Berkeley; Fulvio Parmigiani, Catholic University; Jim Patel, Lawrence Berkeley National Laboratory; Rupert Perera, Lawrence Berkeley National Laboratory; Phil Platzman, Lucent Technologies; Art Robinson, Lawrence Berkeley National Laboratory; George Sawatzky, University of Groningen (Netherlands); John Spence, Arizona State University; Yasuhisa Tezuka, Lawrence Berkeley National Laboratory; Ku-Ding Tsuei, Synchrotron Radiation Research Center; Xingjiang Zhou, Lawrence Berkeley National Laboratory.

(2) Magnetism and Magnetic Materials

Chair: David Awschalom, University of California, Santa Barbara

Facilitators: Jo Stöhr, IBM Almaden Research Center, and Jeff Kortright, Lawrence Berkeley National Laboratory

Technical Advisors: Tony Young and Thomas Stammler, Lawrence Berkeley National Laboratory

Technical Writer: Deborah Dixon, Lawrence Berkeley National Laboratory

Working-group members: Juana Acrivós, San Jose State University; Uwe Arp, National Institute of Standards and Technology; Sam Bader, Argonne National Laboratory; C.T. Chen, Synchrotron Radiation Research Center (Taiwan); Cylón Da Silva, National Synchrotron Light Laboratory (Brazil); Deborah Dixon, Lawrence Berkeley National Laboratory; Charles Fadley, University of California, Davis; Hsueh-Hsing Hung, Synchrotron Radiation Research Center (Taiwan); Yves Idzerda, Naval Research Laboratory; Peter Johnson, Brookhaven National Laboratory; Akito Kakizaki, University of Tokyo (Japan); Sang-Koog Kim, Lawrence Berkeley National Laboratory;

Kannan Krishnan, Lawrence Berkeley National Laboratory; Ki Bong Lee, POSTECH (Korea); Steve Marks, Lawrence Berkeley National Laboratory; William Oosterhuis, U.S. Department of Energy; Stuart Parkin, IBM Almaden Research Center; Z.-Q. Qiu, University of California Berkeley; Bruno Reihl, Paul Scherrer Institut (Switzerland); Mike Scheinfein, Arizona State University; Ivan Schuller, University of California San Diego; Frank Schumann, Lawrence Berkeley National Laboratory; Hans-Christoph Siegmann, ETHZ (Switzerland); Thomas Stammer, Lawrence Berkeley National Laboratory; James Tobin, Lawrence Livermore National Laboratory; Christian Vettier, European Synchrotron Research Facility (France); Dieter Weller, IBM Almaden Research Center; Tony Young, Lawrence Berkeley National Laboratory.

(3) Polymers, Soft Matter, and Biomaterials

Chair: Tom Russell, University of Massachusetts, Amherst

Facilitators: Steve Kevan, University of Oregon and Harald Ade, North Carolina State University

Technical Advisors: Tony Warwick and Simone Anders, Lawrence Berkeley National Laboratory

Technical Writer: Jane Cross

Working-group members: Ben Chu, State University of New York Stony Brook; George Cody, Carnegie Institution of Washington; Steve Gregory, The Dow Chemical Company; Adam Hitchcock, McMaster University; Malcolm Howells, Lawrence Berkeley National Laboratory; Chris Jacobsen, State University of New York Stony Brook; John Kerr, Lawrence Berkeley National Laboratory; Gary Mitchell, Dow Chemical Company; John Pople, Stanford Linear Accelerator Center; Cyrus Safinya, University of California Santa Barbara; Gordon Vrdoljak, University of California Berkeley; Tony Warwick, Lawrence Berkeley National Laboratory; Joe Zasadzinski, University of California Santa Barbara.

(4) Nanostructures and Special Opportunities in Semiconductors

Chair: Marvin Cohen, University of California, Berkeley

Facilitators: Daniel Chemla, University of California, Berkeley, and Franz Himpsel, University of Wisconsin-Madison

Technical Advisors: Simone Anders, Mike Martin, and Scott McHugo, Lawrence Berkeley National Laboratory

Technical Writer: Joe Chew, Lawrence Berkeley National Laboratory

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National Laboratory; Tony van Buuren, Lawrence Livermore National Laboratory; Wladyslaw Walukiewicz, Lawrence Berkeley National Laboratory; Stan Williams, Hewlett-Packard Laboratories.

(5) New Directions in Surface and Interface Science

Chair: Gabor Somorjai, University of California, Berkeley

Facilitators: Chuck Fadley, University of California, Davis, and Michel Van Hove, Lawrence Berkeley National Laboratory

Technical Advisors: Clemens Heske and Eli Rotenberg, Lawrence Berkeley National Laboratory

Technical Writer: Gloria Lawler, Lawler Associates

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(6) Environmental and Earth Sciences

Chair: Gordon E. Brown, Jr., Stanford University

Facilitators: David Shuh and Geraldine Lamble, Lawrence Berkeley National Laboratory

Technical Advisors: Alastair MacDowell and Eddie Moler, Lawrence Berkeley National Laboratory

Technical Writer: John Hules, Lawrence Berkeley National Laboratory

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of California, Berkeley; Satish Myneni, Lawrence Berkeley National Laboratory; George Redden, Stanford University; Donald Reed, Argonne National Laboratory; Joerg Rothe, Lawrence Berkeley National Laboratory; Hans Ruppert, Stanford University; Dale Sayers, North Carolina State University; Roland Schulze, Los Alamos National Laboratory; Paul Smith, U.S. Department of Energy; Lynda Soderholm, Argonne National Laboratory; Don Sparks, University of Delaware; Jeff Terry, Los Alamos National Laboratory; Albert Thompson, Lawrence Berkeley National Laboratory; Tetsu Tokunaga, Lawrence Berkeley National Laboratory; Brian Tonner, University of Wisconsin Milwaukee; Sam Traina, Ohio State University; N. Ulagappan, Lawrence Berkeley National Laboratory; Stephen Wasserman, Argonne National Laboratory; Glenn Waychunas, Lawrence Berkeley National Laboratory; Eric Ziegler, Lawrence Berkeley National Laboratory.

(7) Biosciences

Chair: Graham Fleming, University of California, Berkeley

(a) Protein Crystallography.

Facilitator: Thomas Earnest, Lawrence Berkeley National Laboratory

Technical Advisor: Carl Cork, Lawrence Berkeley National Laboratory

Technical Writer: Doug Vaughan, Lawrence Berkeley National Laboratory

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(b) Soft X-Ray Microscopy.

Facilitator: Werner Meyer-Ilse, Lawrence Berkeley National Laboratory

Technical Advisor: Carolyn Larabell, Lawrence Berkeley National Laboratory

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